TEXT-BOOKS OF PHYSICAL
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THE RELATIONS BETWEEN

CHEMICAL CONSTITUTION

AND SOME

PHYSICAL PROPERTIES

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WITH DIAGRAMS

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PREFACE

As indicated by the title, this volume does not exhaustively treat of the whole subject in question. For various reasons a few physical properties have been omitted from consideration, the more important being Crystalline Form, Optical Rotatory Power, Electric Conductivity, and Heat of Combustion. The relations between the first named of these properties and chemical constitution could not be fully understood without some general account of crystalline structure and the methods of measurement, so that a satisfactory treatment of this subject would occupy so much space as to require a separate volume. The relations between constitution and Optical Rotatory Power, Electric Conductivity, and Heat of Combustion have been thoroughly dealt with in the volumes of this series entitled "Stereochemistry," "Electro-chemistry" (Vol. I.), and "Thermochemistry." Some other physical properties, for example, Solubility, Dielectric Constant, and Magnetic Susceptibility have been omitted because the relations between them and constitution are not yet sufficiently elucidated to call for special treatment. However, it is hoped that these may be included in a future edition.

A book of this kind runs the risk of satisfying neither the physical chemist nor the structural chemist; but it is necessary to point out that it has been written from the standpoint of organic chemistry. This standpoint has been assumed both from necessity and from personal inclination, the former arising from the fact that by far the greater portion of research in this subject has been focussed on the compounds of carbon.

In preparing this volume I have endeavoured to present the numerous independent relations in a connected and readable form ; but I have found that ideal difficult to attain. With this object in view the inclusion of so large a number of tables of numerical data is undesirable; but these seem indispensable, for the validity of the empirical rules described depends chiefly on the scope of the data from which they are deduced. To preserve some method in the order of treatment, the various properties are dealt with under the successive headings of Mechanical, Thermal, Optical, and Electrical properties ; but it is not claimed that this method of classification is perfect. To increase the utility of the book for purposes of reference, the chapters dealing with each physical property have been subdivided into sections which deal with successive portions of the subject. The index is divided into three parts : the usual index of authors' names, a subject index, and an index to the substances mentioned. By this subdivision it is hoped that the reader may be able more rapidly to find the subject or data which he may require. In preparing the last-named index I wish to acknowledge the help of Mr. E. de B. Barnett.

There is no doubt that the relations between physical properties and constitution are becoming more and more employed by the chemist as an aid to resolving the structures of substances which have not yielded to the purely chemical method. To meet the demand which may arise from this source and perhaps to stimulate it, I have inserted at the end of each chapter a section briefly describing the method of applying the relations, and a few typical examples. But while thus bearing in mind the requirements of the research chemist, I have endeavoured to treat the subject so that it may be easily read by the student who possesses a general knowledge of chemistry and of elementary physics.

In obtaining many of the references dealing with the older portions of the subject I wish to acknowledge the help afforded by the larger works of Ostwald and of Graham-Otto.

The book was read in manuscript by Mr. T. P. Hilditch, and in proof by Professor Inglis, Dr. Stewart, and Mr. H. T. Clarke. My thanks are due to these gentlemen, and to Professor Collie, and to Sir William Ramsay, the editor of this series, for many valuable suggestions. Finally, I wish to acknowledge the permission kindly given me by the Publication Committee of the Chemical Society to reproduce with their electrotypes numerous absorption curves from the *Transactions*. The same acknowledgment is due to Dr. Stewart for permission to reproduce absorption curves from " Recent Advances in Inorganic Chemistry."

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CHAPTER I

INTRODUCTION

THE subject treated in this volume is the study of the relations between the numerical values of physical properties and the chemical constitution of the molecule. The question may be approached in two ways. Firstly, we may endeavour to find to what extent the value of the property is determined by the number and kind of atoms present in the molecules of compounds; or, secondly, we may determine how the property is influenced by the mode of linkage of the atoms. The first method may be said to afford an estimate of the "additive" features, whilst the second deals with the "constitutive" nature of the property.

Most physical properties exhibit both additive and constitutive features. The only purely additive property is molecular mass, which is equal to the sum of the masses of the component atoms, and the most constitutive property is optical rotatory power, whose existence depends on a peculiar arrangement of the atoms. It is very difficult to define the relative strength of these characteristics in any physical property; but it may be noted that Ostwald[1] has arranged the more important in the following order of increasing constitutive nature: mass, refractive power, volume relations, magnetic rotation, absorption of light, and optical rotatory power. We might add

[1] *Trans. Chem. Soc.*, **59**, 198 (1891).

fluorescence between absorption and optical rotation, and capillarity and dispersive power at a level with refractivity.

Ostwald[1] has pointed out that besides the additive and constitutive physical properties there is a third type—the " colligative," the numerical value of which depends solely on the number of molecules present. Perhaps the best example of this type of property is gaseous volume, which under ordinary pressures is almost exactly proportional to the number of molecules of the gas present. Since colligative properties are independent of the composition and structure of the molecule, we shall not discuss them in this volume.

Before proceeding to consider in detail the relations between physical properties and chemical constitution, we shall trace the history of their development. The reader will then be able to appreciate the bearing of the subject on the science of pure chemistry, and, perhaps, after reading the ensuing chapters, he will be able to form some estimate of the trend of future research.

The subject which we are about to study is by no means of recent growth ; it is the oldest branch of physical chemistry, and its origin may be traced to the beginning of last century, when the foundations of modern chemistry were being laid. This science, which deals with the relations between physical properties and chemical constitution, may be regarded as an offshoot of pure chemistry ; and we shall find that its development has always depended on the advance of chemical theory. In order to make clear this relation we shall follow the advance of our subject side by side with that of the parent science.

Viewed from a general standpoint, the development of the relations between physical and chemical properties appear to have passed through two phases : the additive and constitutive, and this sequence naturally results from the stages through which chemical science has passed. At the foundation of modern chemistry only the relative proportions of the elements in substances were known, so that research was confined to the question whether the physical properties of a compound can be represented in numerical value as equal to the sum of the

[1] *Lehrbuch der Allgemeinen Chemie,* vol. i. 1120 (1891).

values of the components. It is evident that the majority of chemists then entertained this view.

Throughout all the earlier investigations attempts were made to show not only that the numerical value of the property of the compound is equal to the sum of certain values assigned to the component elements, but also that these preserve the same value, whether free or combined. The responsibility for this view must be laid on Gay Lussac's important discovery of the relations between the volume of a gas and those of its gaseous components. Gay Lussac determined the relative combining volumes of gases, and from their specific gravities he was able to calculate the specific gravity of a compound gas formed from them. This discovery, made in 1805,[1] is the first suggestion that the properties of a compound are numerically related to those of the separate constituents, and it is clear that the idea contains the germ from which the whole of our knowledge on this subject has developed. About the same date Biot and Arago claimed to have proved that the refractive power of a gaseous compound is equal to the sum of the refractivities of the gaseous components, but this was later shown by Dulong[2] to be incorrect.

Progress during the three or four decades following these researches was very slow. In spite of the efforts made by Gay Lussac and Thénard, the methods of analysis were not yet sufficiently accurate to determine the elementary composition of carbon compounds, and thus the work of chemists was confined to the investigation of inorganic substances. The only experiments during this period which need be here noticed are those of Le Royer and Dumas,[3] of Herapath,[4] and of Neumann.[5]

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[1] It may be observed that the previous discoveries of the combining weights of substances are omitted from consideration; mass being a property entirely independent of constitution. The recent researches made by Landolt (*Zeit. Phys. Chem.*, 12, 1820 (1893); 55, 589 (1906), to decide whether substances combine without gain or loss of weight, may be consulted as bearing on this question.

[2] *Ann. Chim. Phys.*, [2] 31, 154 (1826).

[3] *Journ. de Phys.*, 92, 409 (1821).

[4] *Phil. Mag.*, 64, 322 (1823).

[5] *Pogg. Ann.*, 23, 1 (1831).

Le Royer and Dumas attempted to extend Gay Lussac's law to the volumes of solids, and, typifying the current ideas of the period, they calculated the " atomic volumes " of carbonic and sulphuric acids from the densities of lime and its carbonate and sulphate.   Herapath, assuming that the densities of the metals are not altered by combination, endeavoured to calculate the volume of oxygen in the oxides by subtracting from the volumes of the latter, the volumes of the metals contained therein.   The researches of Neumann, which were published in 1831, extended to compounds the law discovered by Dulong and Petit relating to the specific heats and atomic weights of the elements.   The experiments showed that stoichiometrical quantities of different metals have the same heat capacity when combined with the same acid.

The work of Liebig on the analysis of carbon compounds—begun in 1823—laid open the way to a vast field of fresh material.   The growth of organic chemistry then began in earnest, and with it the notion of chemical constitution.   Until about 1840 the attention of chemists was mainly occupied by the advancing theories of chemical constitution.

In 1832 Liebig and Wöhler founded the " radicle " theory on their investigation of benzoic acid and its derivatives, and several years later Dumas and Laurent published their theory of chemical types.   The former experimenters showed that a group of atoms may play the part of an element in a substance ; this group is an unchanging constituent of a series of compounds, and it may be replaced in these compounds by simple bodies.   Dumas, however, preferred to regard compounds as based on a particular type or cluster of atoms from which they may be derived by substitution.

About this time Gerhardt entered upon a series of researches to find some more general system of classification which would embrace the older theories.   We may note that, although he was not at first successful in this object, his earlier work resulted in the introduction of the notion of homology, which was later to play an important part in the search for the numerical relations between physical properties and constitution.

Then came the brilliant researches of Bunsen on cacodyl,[1] of Wurtz[2] and Hofmann[3] on the substituted ammonias, of Williamson[4] on etherification, and of Frankland[5] and Kolbe on the free hydrocarbon radicles. Thus, in 1853, Gerhardt was able to attain the result he had so long desired. From the premise that nearly all chemical change is the result of double decomposition, he deduced that a substance formed during chemical action must consist of two parts: the new one which entered in exchange for that eliminated, and the one which was present in the substance acted upon. These two portions were called residues, they were supposed to be combined or " copulated " with one another by their affinities.

While these advances in chemical theory were being made, the development of the relations between physical and chemical properties entered the second phase, which may be called the constitutive. It now began to be realized that the influence of an element on the physical properties of a compound may vary according to its chemical function. Formerly it was merely the relations between physical properties and elemental composition that had been studied, but now the attention of chemists was first directed to the influence of constitution. This advance was first made by Hermann Kopp, who, in his classical researches on volumes, boiling-points, and specific heats, laid the foundations of the modern portion of our subject.

There is little doubt that Kopp entered on these experiments with the conviction that the physical properties of a compound would prove to be additive, and this certainly was confirmed by his earlier results. Kopp was the first to introduce the methods of calculating the value of the physical property of an element by comparing the values for two compounds of different composition. On comparing the molecular volumes of organic acids with those of the methyl and ethyl esters, he found the constant differences:

[1] *Ann.*, **37**, 1 (1841); **42**, 14 (1842) ; **46**, 1 (1843).
[2] *Ann. Chim. Phys.*, **30**, 443 (1850).
[3] *Ann.*, **74**, 116 (1850).
[4] *Ann.*, **77**, 37 (1851) ; **81**, 73 (1852).
[5] *Trans. Chem. Soc.*, 1, 60 (1863) ; **2**, 263 (1864).

Mol. vol. of methyl ester − mol. vol. of acid   = 23 units
Mol. vol. of ethyl ester − mol. vol. of methyl ester = 19 units

and hence the volume effect of CH_2 in the ethyl esters would be about nineteen units. Also, having found that the volume of a substance remains the same when two atoms of hydrogen are replaced by one of oxygen, he calculated values for carbon, hydrogen, and oxygen, and then proceeded to show that the molecular volume of a substance composed of these elements could be calculated by summation from its elementary composition. However, in 1855, when, it may be noted, the radicle theory was still in vogue, and Gerhardt's views were still unaccepted, we find Kopp stating that the volume of oxygen may vary according to whether it is situated within or without the radicle, and that a similar variation is found in the volume effects of sulphur and nitrogen. This is the first attempt to assign a definite value to the effect of an element under particular chemical conditions. During this period of developing chemical theory, Kopp's ideas on the relations between the boiling-point and chemical composition seem to have undergone a transition from the additive to the constitutive, similar to that previously noticed with volume relations. In his first investigations it is shown that all ethyl esters boil nineteen degrees higher than the corresponding methyl ester, and that replacement of hydrogen by chlorine causes a rise in boiling-point of twenty-five degrees. Isomers were supposed to have exactly the same boiling-point, and the small differences observed were ascribed to the impurity of the samples and the errors of observation. Kopp, however, modified these views in a paper written in 1855, when, owing to the adverse criticism of other chemists, he was obliged to repeat his former work.

Gerhardt's theory of " residues " had scarcely become universally accepted when a further advance into the theory of chemical structure was made by Kekulé. Gerhardt had shown that the older " radicles " of Liebig and the chemical " types " of Dumas could be resolved into the simpler residues, and now Kekulé was to show that the process

of analysis could be pushed still further to the atoms themselves.

The conception of " combining capacity " was an old one ; indeed, Berzelius had applied it to acids and bases in order to explain the combination of these in definite proportions. In later years Gerhardt extended the idea to his theory of residues ; each residue was supposed to be endowed with affinity which enabled it to become copulated with another, but it was further assumed that a residue had only a certain amount of combining affinity available, and it was evidently this which determined the type on which the compound was built. Then Frankland, from his researches on the organo-metallic compounds, made the important deduction that an atom has a definite saturation capacity, which is the same whatever the character of the atoms combined with it may be. This conception served as the foundation on which Kekulé built his theory.

Kekulé, with the aid of Gerhardt's types, began by finding the saturation capacity or "valency" of various elements ; thus potassium, chlorine, bromine, and hydrogen, were shown to be univalent, oxygen and sulphur bivalent, and nitrogen tervalent. From these elements the step to carbon was obvious, and in 1858 Kekulé announced that carbon must be regarded as quadrivalent. This conclusion was formed by comparing the compositions of the simplest carbon compounds, *e.g.* CO_2, $COCl_2$, CCl_4, and $CHCl_3$. It is evident that the smallest quantity of carbon which can enter into combination with other elements always unites with four such quantities of a univalent, or two of a bivalent element. To this discovery of the quadrivalency of carbon Kekulé added the hypothesis of constant valency, and thence developed a new theory of chemical combination. Chemical compounds were now shown to be formed by the mutual saturation of the atomic affinities taken valency by valency. When this theory was applied to compounds rich in carbon it immediately followed that the atoms of this element must be directly united to one another ; thus homology was explained, and at the same time the most important chemical property of carbon was discovered.

It is sufficient for the present purpose merely to notice
that this discovery of the peculiar power of carbon to combine
with itself, led Kekulé to the conception of unsaturated carbon,
and thence, in 1865, to the cyclic structure of aromatic com-
pounds; so that at this date the framework of modern
structural theory was almost complete. Kekulé was also the
first to introduce the graphic method of representing the con-
stitution of substances. He employed a sphere of given size
to represent an equivalent of an element, a bivalent element
was composed of two such spheres fused together, a trivalent,
three, and so on. The formulas produced by this scheme
were somewhat clumsy, so that it was not long before Erlen-
meyer proposed that Berzelius' scheme of employing a letter
to represent an element should be preserved, and lines should
be drawn from it to show the number of valencies and
the manner in which they satisfied the valencies of other
elements.

It is impossible here to give even an outline of the way
in which research after research showed Kekulé's theories to
be correct, and still less to recount the services they have
rendered to organic chemistry. Instead, we shall now turn
once again to the relations between physical properties and
chemical constitution, and briefly follow their development
during the twenty years—from 1850–1870.

In this period, and especially during the later part of it, the
chief features to be observed are the stimulus given to research
by the expansion of organic chemistry, and the increasing
attention paid to the effect of constitution. Until about
1860 Kopp remained almost the sole worker in the field, but,
as we have already seen, he had, by 1855, become convinced
of the influence of constitution on the molecular volumes and
boiling-points of organic substances. In a paper which
appeared [1] in 1865 he gave an account of his researches on
the specific heat of inorganic compounds; but here no evidence
was found of the constitutive nature of the property, since the
elements were shown to have the same atomic heats whether
combined or in the free condition. In 1863 Gladstone and

[1] *Ann. Suppl.*, **3**, 289 (1864–5).

Dale published the first[1] of a series of researches on the refractivity of compounds, in which they clearly showed that this property was influenced by constitution. They found that isomeric compounds have the same refractive power only if their chemical nature is the same, and isomerides of widely different nature have different refractive powers. In the next year Landolt[2] drew attention to the additive nature of this property by showing that the effect of homology is constant, and that isomeric esters and acids have approximately the same molecular refractive power. Gladstone and Dale continued to lay stress on the influence of constitution, and in 1870 they found[3] that compounds rich in carbon, such as aromatic substances, have an abnormally high refractivity. During this period research was extended to other physical properties, and in nearly all these the influence of constitution was detected. Mendeléeff, in 1860, performed the first researches[4] on the connection between surface tension and composition; but he seems to have been inclined to regard this property as additive, since he claimed that the molecular cohesion of homologues increases regularly from member to member. Then Buff,[5] in 1865, expanded the work begun by Kopp on the volumes of organic substances. He clearly showed that the volume effect of a combined element varies with the degree of saturation. His calculation of the volume effect of unsaturated carbon is noteworthy as the earliest attempt to assign a value to this element in the unsaturated state, and here the influence of Kekulé's work is seen for the first time. This influence is also evident in the work[6] of Rellstab (1868), who showed that unsaturated compounds have a greater viscosity than the saturated, and in that of Hinrichs,[7] who found that the volatility of a substance is

[1] *Phil. Trans.*, **153**, 319 (1863).
[2] *Pogg. Ann.*, **123**, 595 (1864).
[3] *Proc. Roy. Soc.*, **18**, 49 (1869-70).
[4] *Compt. Rend.*, **50**, 52 ; **51**, 97 (1860).
[5] *Ann. Suppl.*, **4**, 129 (1865).
[6] *Dissertation, Bonn*, 1868.
[7] *Chem. Jahresber.*, 1868, p. 10.

greater if the carbon atoms are arranged in the form of a branched chain than when these form a normal chain.

1870 AND ONWARDS

Since the work of Kekulé the basis of our ideas of chemical structure has remained unaltered, but the theory has been expanded in two directions. While the structural theory was being developed, Pasteur discovered [1] the optically active tartaric acids, and their relation to the inactive racemic acid. Kekulé recognized that these substances have the same chemical structure, but he was content to call them " physical isomerides." Other cases of isomerism of a similar nature were then discovered, and, in 1873, Wislicenus, having added to these the isomeric lactic acids, pointed out [2] that the formulæ then used for them merely represented the atoms of a molecule as lying in one plane. He proposed that instead some method of showing their arrangement in space should be employed. It was not long before this improvement came, for in 1874 Le Bel and van't Hoff independently offered an explanation of the isomerism upon this basis. The theory propounded by van't Hoff was an extension of Kekulé's law of the quadrivalency of carbon : the four valencies were supposed to be directed to the corners of a tetrahedron at the centre of which the carbon atom is situated. Thence it followed that when four different groups are attached to the same carbon atom, there may exist three isomerides of which two differ from one another only in the opposed spatial order of the groups, whilst the third is formed by combination or mixture of the others. It was further established that optical rotatory power, which is the distinguishing property of the two " opposed " isomers, occurs only in substances containing the " asymmetric " carbon atom. We see, then, that these researches led to the discovery of the relation between chemical constitution and optical rotatory power which is perhaps the most constitutive property.

[1] *Compt. Rend.*, **85**, 180 (1852).
[2] *Ann.*, **167**, 1343 (1873).

Stewart, in considering the recent progress of organic chemistry, has remarked [1] that the distinctive feature of the past twenty-five years has been the growth of dynamical theories of molecular structure. The insufficiency of the statical conception of the molecule was felt shortly after the structural theory was established, and Kekulé was the first to bring forward the required modification. Ladenburg had objected [2] to the formula for benzene on the grounds that no isomerides of the ortho-disubstituted compounds were known, whereas according to Kekulé's scheme two should exist—
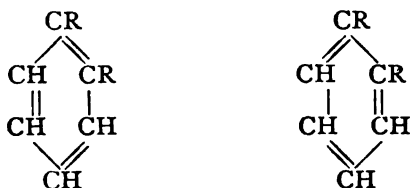
Kekulé met this objection by assuming that the carbon and hydrogen atoms of benzene are vibrating so as to collide repeatedly. Thence, with certain assumptions as to the nature of valency, it followed that the structure of the molecule is continually passing from—
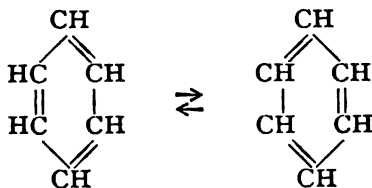
and *vice versâ*, so that the isomerides in question would not exist.

Dynamic hypotheses have since been advocated on other grounds. There are many substances which cannot be satisfactorily represented by the ordinary structural formulæ, since they react sometimes according to one structure and

[1] *Recent Advances in Organic Chemistry*, 1908.
[2] *Ber.*, **2**, 140 (1869).

sometimes according to another. Laar,[1] recognizing that in many cases the alternative structures differed merely by the position of a hydrogen atom, supposed that this atom is vibrating between the two positions. Such compounds were called tautomeric.

Bischoff,[2] while studying the formation of carbon chains, observed that reactions which normally should give a chain of five or six carbon atoms, often take an abnormal course. To explain these exceptions Bischoff put forward his " Dynamic Hypothesis," in which the spatial and dynamic views of constitution were combined. According to stereo-chemical notions the end carbon atoms of a five or six membered carbon chain lie close together, and it is evident that these, when vibrating, will collide more frequently than the carbon atoms of a shorter chain. The abnormal cases are readily explained by supposing that a reaction tends to avoid a product in which interatomic collisions are exceptionally frequent.

The most recent dynamical theory is that of Knoevenagel [3] who has assumed that the carbon atoms in certain compounds are endowed with a rolling motion. The development of this hypothesis is too complicated to be followed here, but we may observe that it fully accounts for the properties of a conjugated system of ethylenic linkages, and it explains the existence of certain isomeric forms of benzene derivatives. The latter have hitherto been regarded as polymorphous, or merely as " physical isomerides," just as optical isomerides were treated before stereochemical theory was introduced. Knoevenagel terms them " moto-isomerides."

It cannot be said that the development of the relations between chemical constitution and physical properties kept pace with this rapid advance of the theory of chemical structure. In 1876 a relation between fusibility and constitution was detected by Markownikoff,[4] who found that the melting-point

[1] *Ber.*, **18**, 648 (1885) ; **19**, 730 (1886).
[2] *Ber.*, **24**, 1087 (1891).
[3] *Ber.*, **36**, 2806 (1903).
[4] *Ann.*, **182**, 340 (1876).

is raised by converting a normal to a branched chain of carbon atoms. Shortly afterwards Baeyer[1] (1877) observed the alternating effect of homology, and then Carnelley[2] discovered that the fusion temperature of symmetrical compounds is higher than that of less symmetrical isomerides. Research was also extended to many more important properties.

In 1879 the absorption spectra of organic compounds were first systematically examined. Soret and Rilliet, investigating homologous compounds, found[3] that the ultra-violet absorption of the alkyl nitrates continually shifts towards the red end of the spectrum when successive methylene groups are introduced. In the same year Hartley published the first[4] of his extensive researches on ultra-violet absorption. This work is of peculiar interest, since it showed that the absorption is closely connected with the dynamic properties of the molecule. Hartley insisted on the constitutive nature of this property, but a few years later Abney examined[5] infra-red absorption, and found that here additive relations hold. About the same date a connection between fluorescence and constitution was first indicated by Liebermann,[6] but the dynamic character of the property was not firmly established until the theories of Lommel[7] were published.

In 1880 the relations between refractivity and chemical constitution were developed by the important work of Brühl,[8] who showed that the refractivity of an element varies under different structural conditions. Moreover, Brühl calculated the atomic refractivities for ethylenic and acetylenic carbon, and for ketonic, hydroxylic, and ethereal oxygen, and then showed that the molecular refractive power of a compound may be calculated from the sum of these atomic refractivities if the correct allowance be made for the structural conditions.

[1] *Ber.*, **10**, 1286 (1877).

[2] *Phil. Mag.*, [5] **13**, 116 (1882).

[3] *Compt. rend.*, **89**, 747 (1879).

[4] Hartley and Huntington, *Proc. Roy. Soc.*, **28**, 223 (1879).

[5] *Proc. Roy. Soc.*, **31**, 416 ; **32**, 483 (1881).

[6] *Ber.*, **13**, 913 (1880).

[7] *Wied. Ann.*, **8**, 244 (1878) ; **24**, 288 (1885).

[8] *Ann.* **203**, 1 (1880).

Thus the additive and constitutive features of the property were simultaneously developed.

Then, in 1882, W. H. Perkin, sen., completed the first[1] of a series of important researches on magnetic rotation. These earlier experiments showed that the property is very sensitive to structural changes, but additive relations—*e.g.* the constant effect of homology—could be clearly detected. In his later work Perkin studied these features side by side, and employed them to determine the constitution of organic compounds.

In 1884 the relations between surface tension and composition were earnestly studied by Schiff,[2] who found that the molecular effect could be represented as the sum of atomic constants. The property would thus seem to be additive, but the conclusion cannot be regarded as final, since later work seems to show that the property is influenced by constitution. Schiff did not pursue the subject.

Von Reis,[3] in 1881, was the first to demonstrate the constitutive nature of the specific heat of organic compounds, and his deductions were on the whole confirmed by the observations of Schiff[4] in 1886.

Some further work on viscosity was carried out in 1878–1881 by Pribram and Handl,[5] who compared the viscosities of isomeric compounds. The rule previously advanced by Guerout[6] (1875), that "isomerides" have the same viscosity, was shown to be merely an approximation. This and other results obtained by Pribram and Handl made evident the effect of constitution, but the subject remained in an unsatisfactory state for many years, until Thorpe and Rodger,[7] by their more accurate measurements, clearly defined the influence of constitution on viscosity.

We have now passed in review the chief researches which

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[1] *Trans. Chem. Soc.*, **45**, 465 (1884).

[2] *Ann.*, **243**, 47 (1884).

[3] *Wied. Ann.*, **13**, 447 (1881).

[4] *Ann.*, **234**, 300 (1886).

[5] *Wien. Ber.*, **78**, 113 (1878).

[6] *Compt. rend.*, **81**, 1025 (1875).

[7] *Phil. Trans.*, **185**, 397 (1894).

brought the development of our subject up to the level of the general theories of chemical structure. It is unnecessary to give an outline of the researches which followed these from about 1890 to the end of last century, since in that interval chemists merely filled in the details of the schemes laid down by the pioneers. The modern developments of the relations between chemical and physical properties will be considered in the concluding chapter, since, being acquainted with the chief facts, we shall then be able to take a general survey of the present position, and perhaps obtain a glimpse into the future.

It must not be imagined that chemists have so eagerly pursued this subject merely with the object of establishing empirical relations between physical properties and chemical constitution. Generally speaking, in all these researches there has been the ulterior motive of applying these relations, when once firmly established, to determining the constitution of organic compounds ; but it must be admitted that this has been attained only with a few properties, such as refractive power and magnetic rotation. The physical properties which are best suited for this application are those on which the influence of constitution is moderately pronounced, but yet is subordinate to the additive character, that is to say, when the numerical effects of special types or changes of constitution are constant for all compounds.

The ideal method of determining the constitution of a substance is to calculate the molecular value of the property from the sum of the atomic effects modified according to the suspected structure ; if the resulting value agrees with that found by experiment, the structure is confirmed. This method, however, is an ideal one, and can be applied only with refractivity, dispersive power, and perhaps viscosity ; with more constitutive properties the process employed is often not quite so straightforward, and the results not so trustworthy. The particular method adopted with each physical property, and the data on which it is based, are fully described in the following chapters. It is important to remember that evidence drawn from physical properties should be regarded as subordinate to chemical evidence.

MECHANICAL PROPERTIES

CHAPTER II

CAPILLARITY

§ 1. *SURFACE TENSION*

THE phenomena of capillarity have been known to physicists for some centuries, indeed, the discovery of them is attributed [1] to Leonardo da Vinci. The first quantitative measurements were made by Jurin,[2] who correctly showed that the height to which a liquid rises in a capillary tube is inversely proportional to the diameter of the latter. This observation gave impetus to the theoretical development of the subject, which at the opening of last century rapidly advanced under the efforts of Laplace, Poisson, Young, and Gauss.

Laplace [3] (1805) assumed that liquids are homogeneous, and that an attractive force is mutually exerted between the component particles. He further supposed that the attraction between any two particles is a function of the distance between them, being very intense when the distance is small but diminishing very rapidly as this is increased. At a certain finite distance, l, the force becomes vanishingly small. It is clear that the forces exerted on a particle situated in the body of the liquid will neutralize one another, so that the resultant force is equal to zero. On the other hand, particles which are at a distance less than l from the surface will be subject to a force acting inwardly and normally to the surface. Thus if

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[1] See *Pogg Ann.*, **101**, 551 (1860).
[2] *Phil. Trans.*, **80** (1718).
[3] *Oeuvres*, vol. iv. 389, Paris (1845).

AB is the plane surface of a liquid and *m* a particle at a less distance than *l* from the surface, then the circle of radius *l* (Fig. 1), will represent the sphere of action of *m*. It is evident that the forces exerted on *m* by the particles in the area ABCD will neutralize one another, whilst those due to the particles in the area DEC (equal to AFB) will result in a force acting inwardly from AB. It follows that the outer layer of the liquid is in a state of tension which acts so as to reduce the area of the surface and
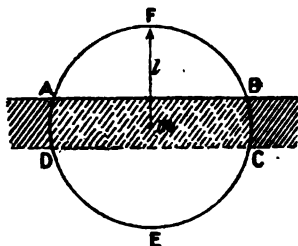
FIG. 1.

resists any attempt to enlarge it, consequently the liquid behaves as though it were enclosed in an elastic skin. This conclusion leads to the idea that a tension exists along the surface of a liquid,[1] and Young developed a theory of capillarity on this assumption. Surface tension is measured as a force which acts normally along a line of unit length on the surface of the liquid, and it is usually represented by the symbol γ.

There are many methods by which the surface tension may be determined, but since the greater part of the data which we shall consider have been derived from either of two we need deal with these only. The following is a very brief outline of the principles on which they are based.

1. *The Rise of Liquids in the Capillary Tubes.*—When a circular capillary tube is dipped vertically into a liquid the level of the latter rises in the tube until a position of equilibrium is reached; the weight of the liquid column is then balanced by the surface tension. If the surface of the liquid makes the angle θ at the point of contact with the inner wall of the capillary tube, the vertical component of γ will be $\gamma \cos \theta$.

We may then write

$$\gamma \cos \theta 2\pi r = \pi r^2 h d \quad . \quad . \quad . \quad . \quad \text{I.}$$

[1] Thomas Young, *Phil. Trans.*, **95**, 65 (1805).

where r = radius of the tube in centimetres ;
  h = height (in cms.) of the liquid column ;
  d = density of the liquid.

If, as may be assumed[1] in most cases, the liquid completely wets the tube, then $\theta = 0$, and we have—

$\gamma = \frac{1}{2}rhd$ in grams weight per centimetre . . II.

In I. the weight of the meniscus is neglected ; to correct[2] for this omission the value $\frac{r}{3}$ may be added to h, then—

$$\gamma = \frac{dr}{2}\left(h + \frac{r}{3}\right)$$

For the experimental application of this method the reader should consult the work of Ramsay and Shields.[3]

2. *The Weight of Falling Drops.*—The measurement of surface tension by the weight of falling drops seems to have been first undertaken by Tate ;[4] the method was subsequently developed by Quincke,[5] Duclaux,[6] and Lord Rayleigh.[7] If a sufficiently long tube of narrow bore is filled with liquid and placed in a vertical position, a drop will form at the lower orifice. If, further, the size of the drop increases, a condition will be reached when the weight can no longer be supported by the surface tension of the liquid ; the drop then falls. If W be the weight of the drop at this moment, we may write—

$$W = 2\pi r\gamma, \quad \text{or } \gamma = \frac{W}{2\pi r}. \quad . \quad . \quad . \quad \text{III.}$$

[1] Whether this is permissible is discussed by Feustel, *Drud. Ann.*, **16**, 61 (1905).

[2] Laplace, *Oeuvres*, iv. 389 (1845), Paris.   See also Poisson, *Nouvelle Théorie de l'action capillaire*, (1831) ; and Hagen, *Pogg. Ann.*, **67**, 1 (1846), for a more accurate correction.

[3] *Zeit. Phys. Chem.*, **12**, 433 (1893).

[4] *Phil. Mag.*, [4] **27**, 176 (1864).

[5] *Pogg. Ann.*, **134**, 356 (1868); **135**, 621 (1868); **138**, 141 (1869) ; **139**, 1 (1870).

[6] *Ann. Chim. Phys.*, [5] **13**, 75 (1878).

[7] *Phil. Mag.*, [5] **48**, 321 (1899).   The method has been criticized by Guye and Perrot, *Archives des Sci. Phys. et Nat.*, [4] **11**, 225 (1901).

Neither of these methods yields results of the highest accuracy; perhaps the best plan of measuring γ is to determine the pressure in an air-bubble formed in the liquid; but for an account of this and other methods a text-book of physics must be consulted.

Besides γ another constant is sometimes employed; it is called specific cohesion, and is usually denoted by a^2. The relation between a^2 and γ is expressed as follows:—

$$a^2 = \frac{2\gamma}{d} = \text{specific cohesion}$$

Whence—since $\gamma = \frac{1}{2}rhd$—it is seen that the specific cohesion is measured by the height to which a liquid rises in a capillary tube of unit radius. The product of specific cohesion and the molecular weight of the liquid has been called molecular cohesion—

$$a^2M = \text{molecular cohesion}$$

If we imagine the volume (MV) of a gram-molecule of a liquid to be in the shape of a cube, then $(MV)^{\frac{1}{3}}$ will represent one edge of this and will show for different liquids the lengths over which equal numbers of molecules are distributed. The value of $\gamma(MV)^{\frac{1}{3}}$ for different substances will therefore be a measure of the surface tension exerted by equal numbers of their molecules; it may be called the molecular surface tension.

Molecular Surface Energy.—In establishing a liquid surface work is done against surface tension, and thus the surface acquires potential energy. If we imagine a liquid film to be enlarged by moving the boundary of breadth d from the position A through the distance l to A', then the work done or the gain in energy of the surface will be γdl.
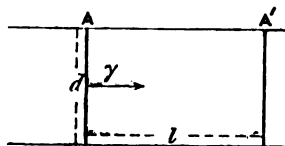
FIG. 2.

Stating this in general terms we may say that the energy of

, a liquid surface is equal to the product of the surface tension and its area—

$$\gamma A = \text{surface energy}$$

If, as before, MV is the molecular volume, then the value of $(MV)^{\frac{2}{3}}$ for different liquids will represent an area over which an equal number of molecules are spread. Hence—

$$\gamma(MV)^{\frac{2}{3}} = \text{relative molecular surface energy}$$

§ 2. *THE INFLUENCE OF TEMPERATURE*

Surface tension decreases with rising temperature until the critical point is reached, when liquid and vapour become identical and the surface tension is zero. Brunner [1] apparently was the first to show that the decrease in capillarity is regular and that it may be represented as a linear function of the temperature thus :—

$$\gamma t = \gamma^{\circ}(1 - ct)$$

in which γt and γ° are the surface tensions at t° and 0° respectively and c is a constant. The same conclusion has been formed by many others,[2] but it is not strictly true. The extensive measurements of Ramsay and Shields [3] show that whilst the above relation holds sufficiently well over small ranges of temperature, as a general expression it is not accurate. This is illustrated by the table on p. 21.

It is doubtful whether the effect of temperature is related to the chemical constitution of the liquid ; Gossart [4] claims that the temperature coefficient is the same for substances of the same class, though his measurements deal only with the alcohols, acids, esters, and some chlorine derivatives ; on the other hand Hock [5] finds no such relation.

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[1] *Pogg. Ann.*, **70**, 485 (1847).

[2] See especially Timberg, *Wied. Ann.*, **30**, 545 (1887); Jäger, *Wien. Ber.*, **101**, 159, 954 (1892) ; Pellat, *Compt. Rend.*, **118**, 1193 (1894) ; Hock, *Wien. Ber.*, **108**, 1516 (1900).

[3] *Zeit. Phys. Chem.*, **12**, 454 (1893).

[4] *Ann. Chim. Phys.*, [6] **19**, 173 (1890).

[5] *Wien. Ber.*, **108** (2A), 1516 (1900).

TABLE I.

ETHYL ETHER.

Temp.	γ in dynes per cm.	Difference for 10°.	Temp.	γ in dynes per cm.	Difference for 10°.
20°	16·49	½ × 2·44	120°	5·65	
40	14·05	1·11	130	4·69	0·96
50	12·94	1·14	140	3·77	0·92
60	11·80	1·08	150	2·88	0·89
70	10·72	1·05	160	2·08	0·80
80	9·67	1·04	170	1·33	0·75
90	8·63	1·00	180	0·64	0·69
100	7·63	1·00	190	0·16	0·48
110	6·63	0·98	194·5	0·00	2 × 0·16
120	5·65				

ETHYL ACETATE.

20	23·60	¼ × 7·28	160	7·48	
80	16·32	1·18	170	6·47	1·01
90	15·14	1·16	180	5·51	0·96
100	13·98	1·14	190	4·54	0·97
110	12·84	1·09	200	3·64	0·90
120	11·75	1·09	210	2·80	0·84
130	10·66	1·09	220	1·96	0·84
140	9·57	1·05	230	1·18	0·78
150	8·52	1·04	240	0·49	0·69
160	7·48		245	0·21	2 × 0·28

BENZENE.

80	20·28	1·12	180	9·15	
90	19·16	1·14	190	8·16	0·99
100	18·02	1·16	200	7·17	0·99
110	16·86	1·15	210	6·20	0·97
120	15·71	1·14	220	5·25	0·95
130	14·57	1·12	230	4·32	0·93
140	13·45	1·09	240	3·41	0·91
150	12·36	1·09	250	2·56	0·85
160	11·29	1·07	260	1·75	0·81
170	10·20	1·05	270	0·99	0·76
180	9·15		280	0·29	0·70

§ 3. *SURFACE ENERGY AND TEMPERATURE*

Eötvös[1] pointed out that the molecular surface energy of an unassociated liquid is a linear function of the temperature, and to express this relation he proposed the formula—

$$\gamma(MV)^{\frac{2}{3}} = (T' - T)K$$

in which T' is the critical temperature or the temperature at which surface energy becomes zero, and T the temperature of observation. Ramsay and Shields,[2] however, measured the surface energy of several liquids from the atmospheric to the critical temperature and found that the linear relation does not hold continuously up to the critical point as assumed by Eötvös, but ceases a short distance below it. When $\gamma(MV)^{\frac{2}{3}}$ is
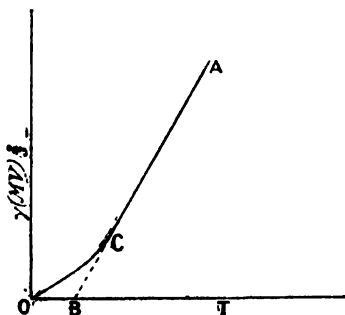
FIG. 3.

plotted out against the temperature measured downwards from the critical, a curve resembling that shown in Fig. 3 is obtained.

In the diagram O represents the critical temperature and T

[1] *Wied. Ann.*, **27**, 448 (1886).

[2] *Zeit. Phys. Chem.*, **12**, 433 (1893), and *Journ. Chem. Soc.*, **63**, 1089 (1893) ; also Ramsay and Aston, *Zeit. Phys. Chem.*, **15**, 89 (1894) ; *Proc. Roy. Soc.*, **56**, 162 (1894) ; Guye and Baud, *Arch. des Sci. ·Phys. et Nat.*, [4] **11**, 449, 537 (1901) ; Dutoit and Friedrich, *Arch. des Sci. Phys. et Nat.*, [4] **9**, 105 (1900).

the difference between this and the temperature of measurement. The curve OCA is straight beyond C and if the linear portion be produced it will cut the temperature axis at a point B below the critical. The linear relation between molecular surface energy and temperature now becomes

$$\gamma(MV)^{\frac{2}{3}} = K\ (T - d)$$

where d is the intercept OB on the temperature axis. For most liquids d is about six degrees. The constant K represents the rate of change in molecular surface energy over the linear portion of the curve, and when $\gamma(MV)^{\frac{2}{3}}$ is measured in dynes per centimetre, the value of K is about 2·12.

The closeness with which this expression fits the experimental data is shown below for benzene and carbon tetrachloride.

TABLE II.

BENZENE $\gamma(MV)^{\frac{2}{3}} = 2\cdot104(T - 6\cdot5)$.

Measured at	T	$\gamma(MV)^{\frac{2}{3}}$ calculated. Ergs.	$\gamma(MV^{\frac{2}{3}})$ observed. Ergs.	Measured at	T	$\gamma(MV)^{\frac{2}{3}}$ calculated. Ergs.	$\gamma(MV^{\frac{2}{3}})$ observed. Ergs.
80	208·5	425·1	425·1	180°	108·5	213·8	214·6
90	198·5	404·5	404·0	190	98·5	193·4	193·6
100	188·5	384·0	383·0	200	88·5	172·5	172·5
110	178·5	362·9	361·9	210	78·5	151·9	151·5
120	168·5	341·6	340·9	220	68·5	131·0	130·5
130	158·5	230·3	319·8	230	58·5	110·1	109·0
140	148·5	299·0	298·8	240	48·5	89·0	88·4
150	138·5	278·1	277·8	250	38·5	68·7	67·3
160	128·5	256·9	256·7	260	28·5	48·6	46·3
170	118·5	235·2	235·7	270	18·5	28·8	25·3

CARBON TETRACHLORIDE $\gamma(MV)^{\frac{2}{3}} = 2\cdot105(T - 6\cdot0)$.

Measured at	T	$\gamma(MV)^{\frac{2}{3}}$ calculated. Ergs.	$\gamma(MV^{\frac{2}{3}})$ observed. Ergs.	Measured at	T	$\gamma(MV)^{\frac{2}{3}}$ calculated. Ergs.	$\gamma(MV^{\frac{2}{3}})$ observed. Ergs.
80	203	414·6	414·7	180	103	204·8	204·2
90	193	393·7	393·7	190	93 ·	183·3	183·2
100	183	372·3	372·6	200	83	162·3	162·1
110	173	351·7	351·6	210	73	140·8	141·1
120	163	330·3	330·5	220	63	118·9	120·0
130	153	309·4	309·5	230	53	96·8	99·0
140	143	288·1	288·4	240	43	76·5	77·9
150	133	267·4	267·4	250	33	53·5	56·8
160	123	246·7	246·3	260	23	35·9	35·8
170	113	226·0	225·3	270	13	21·7	14·7

Turning to associated substances, we find that the value of K varies with temperature, and is smaller than 2·12 ; the molecular surface energy is then no longer a linear function of the temperature. The example of alcohol is quoted in Table III., the fourth column contains the value (K) of the differential $\dfrac{d[\gamma(MV)^{\frac{2}{3}}]}{dt}$ over each interval.

TABLE III.

ETHYL ALCOHOL.

Measured at	τ	$\gamma(MV)^{\frac{2}{3}}$ Ergs.	$\dfrac{d[\gamma(MV)^{\frac{2}{3}}]}{dt}$	Measured at	τ	$\gamma(MV)^{\frac{2}{3}}$ Ergs.	$\dfrac{d[\gamma(MV)^{\frac{2}{3}}]}{dt}$
20°	223·1	331·0		160°	83·1	147·2	
40	203·1	307·3	1·18	180	63·1	112·6	1·73
60	183·1	284·8	1·12	190	53·1	94·9	1·77
80	163·1	261·2	1·18	200	43·1	75·7	1·92
100	143·1	235·0	1·31	210	33·1	57·1	1·86
120	123·1	208·0	1·35	220	23·1	39·2	1·79
140	103·1	178·8	1·46	230	13·1	19·8	1·94
160	83·1	147·2	1·58	240	3·1	3·7	1·61

The cause of the reduction in the value of K is apparent when it is considered that association must increase the total number of molecules in a given volume, and hence the volume occupied by a gram-molecule will be smaller. Thus, one of the factors—$(MV)^{\frac{2}{3}}$—of the molecular surface energy will be diminished, and the rate of change in molecular surface energy will alter in a corresponding degree. Suppose, for example, that MV is the volume occupied by a gram-molecule in the unassociated state, then if the liquid be rearranged into groups of x molecules, the value of MV will become $\dfrac{MV}{x}$ or the "molecular surface" $\left(\dfrac{MV}{x}\right)^{\frac{2}{3}}$. The rate of fall in molecular surface energy will now be

$$\dfrac{d\left[\gamma\left(\dfrac{MV}{x}\right)^{\frac{2}{3}}\right]}{dt} = K$$

whereas in the unassociated state this is represented by

$$\frac{d[\gamma(MV)^{\frac{2}{3}}]}{dt} = 2 \cdot 12$$

hence—

$$\frac{2 \cdot 12}{K} = x^{\frac{2}{3}}, \quad \text{or } x = \left(\frac{2 \cdot 12}{K}\right)^{\frac{3}{2}} \text{ approximately}$$

From this relation it is clear that the value of K may be employed to calculate the association factor of a liquid. In practice all that is necessary is to determine the molecular surface energy at two different temperatures a sufficient distance apart, and then to calculate the value of the differential $\frac{d[\gamma(MV)^{\frac{2}{3}}]}{dt}$ over that interval. The average value of x between the two temperatures is obtained from the equation shown above. Some examples will serve to make this clear; the following are selected from the measurements of Ramsay and Shields.

CS_2, *Carbon disulphide.*—

$$\gamma(MV)^{\frac{2}{3}} \text{ in ergs at } 19 \cdot 4° \text{ C.} = 515 \cdot 4$$
$$\gamma(MV)^{\frac{2}{3}} \text{ in ergs at } 46 \cdot 1° \text{ C.} = 461 \cdot 4$$
$$\frac{d[\gamma(MV)^{\frac{2}{3}}]}{dt} = \frac{515 \cdot 4 - 461 \cdot 4}{46 \cdot 1 - 19 \cdot 4} = \frac{54 \cdot 0}{26 \cdot 7} = 2 \cdot 02$$

Since this value is very close to the normal $2 \cdot 12$, we may conclude that carbon disulphide is unassociated at these temperatures.

HCOOH, *Formic acid.*—

$$\gamma(MV)^{\frac{2}{3}} \text{ in ergs at } 16 \cdot 8° \text{ C.} = 424 \cdot 4$$
$$\gamma(MV)^{\frac{2}{3}} \text{ in ergs at } 46 \cdot 4° \text{ C.} = 397 \cdot 1$$

hence—

$$\frac{d[\gamma(MV)^{\frac{2}{3}}]}{dt} = 0 \cdot 902$$

and

$$x = \left(\frac{2 \cdot 12}{0 \cdot 90}\right)^{\frac{3}{2}} = 3 \cdot 6$$

The average molecular weight of the acid under these conditions is therefore about 3·5 (CH_2O_2).

This method of determining the degree of association of a liquid is based on the assumption that the liquids which give the normal value for K are unassociated. Their molecular weight is supposed to be the same as in the gaseous state. This assumption is supported by the constancy in the value of K with increasing temperature up to a short distance from the critical point; for if the liquids were associated, the complexes would undoubtedly break up, and the value of K consequently alter before this stage was reached. It is further strengthened by the fact that if the "normal" liquids contained complex molecules, the degree of association in each must be the same, for the value of K is almost equal in all cases; such a concurrence is very improbable.[1]

The method has been applied not only to substances which are liquid at the ordinary temperature, but also to fused salts and liquefied gases. Baly and Donnan[2] find the following values for K with liquid oxygen, nitrogen, argon, and carbon monoxide :—

Oxygen	1·91	70–90° (abs.)
Nitrogen	2·00	70–90° (abs.)
Argon	2·02	84–89° (abs.)
Carbon monoxide	1·99	70–90° (abs.)
Carbon dioxide	2·22	249–293° (abs.)
Nitrous oxide	2·2	248–293° (abs.)

The data for carbon dioxide and nitrous oxide were obtained by Verschaffelt.[3]

Bottomley[4] showed that fused potassium nitrate gave 0·445, and sodium nitrate 0·5 for K, hence in the liquid state about ten simple molecules of these salts are associated. Some fused metals have been examined by Siedentopf,[5] who

[1] *Zeit. Phys. Chem.*, 15, 103 (1894); for an improved method, see Ramsay, *Zeit. Phys. Chem.*, 15, 111 (1894).

[2] *Journ. Chem. Soc.*, 81, 907 (1902).

[3] *Beiblätter*, 19, 859 (1895).

[4] *Journ. Chem. Soc.*, 83, 1421 (1903): see also Lorenz; *Ber.*, 41, 3727 (1908).

[5] *Wied. Ann.*, 61, 265 (1897).

proved mercury, bismuth, lead, cadmium and tin to be associated; the values for K were as follows :—

Hg . . 0·65   Pb . . 0·77   Sn . . 0·81
Bi . . 0·50   Cd . . 1·50

These results are especially interesting, since Ramsay[1] and Meyer[2] have shown lead, cadmium and tin to be monatomic in mercury solution; and it is therefore evident that mercury acts as a dissociating solvent with these metals.

In many cases it is found that the molecular aggregates break down at higher temperatures; this can be seen with ethyl alcohol (Table III.) where the value of K rises from 1·1 at the ordinary temperature to about 1·9 at 240° C.; at this temperature the liquid approaches the monomolecular state.

The appended list, which shows the values of K obtained with different liquids, is divided into two parts, containing unassociated and associated substances.

TABLE IV.
UNASSOCIATED LIQUIDS.

Substance.	K	Substance.	K	Substance.	K
CS_2 . . .	2·04	nC_6H_{14}.	2·21	C_6H_6 . . .	2·10
N_2O_4. . .	2·11	$(C_2H_5)_2O$	2·01	C_6H_5CHO .	2·16
$SiCl_4$. . .	2·03	C_2H_5SH	2·06	$C_6H_5NO_2$.	2·23
PCl_3 . . .	2·09	CH_3COCl	2·04	$C_6H_5NH_2$.	2·05
S_2Cl_2 . . .	2·19	CH_3NCS	2·07	C_6H_5CN .	2·16
$Ni(CO)_4$. .	2·30	$CH_3COC_2H_7$. . .	2·04	$C_6H_5OCH_3$.	2·35
CCl_4 . . .	2·21	CH_3COCH_2COOEt	2·18	C_5H_4N . .	2·22
C_2H_5I . .	2·10	$ClCOOC_2H_5$. . .	2·04	C_9H_7N . .	2·43

ASSOCIATED LIQUIDS.

Substance.	K	T interval.	Substance.	K	T interval.
Water	0·89	10–20°	Formic acid . . .	0·90	17–46°
CH_3OH . . .	0·93	16–46°	Acetic acid . . .	0·90	16–46°
C_2H_5OH . . .	1·08	16–46°	Propionic acid . .	1·44	16–46°
C_3H_7OH . . .	1·23	16–46°	Butyric acid . . .	1·57	15–46°
C_4H_9OH . . .	1·36	17–46°	Isobutyric acid . .	1·66	16–46°
CH_3COCH_3. .	1·82	17–46°	$CH_3NH . COOC_2H_5$	1·56	56–101°
C_2H_5CN . . .	1·45	17–46°	Valeroxime . . .	1·72	16–152°
$C_2H_5NO_2$. . .	1·64	17–46°	Glycol	1·03	17–46°

[1] Zeit. Phys. Chem., 8, 360 (1889).   [2] Zeit. Phys. Chem., 7, 484 (1891).

On glancing over the first division of this table, it will be seen that the value of K for normal substances is not strictly constant, evidently it is influenced by constitution.   Thus Ramsay and Miss Aston[1] have drawn attention to the fact that addition of CH_2 to a molecule increases the value of K.   The relation may be illustrated by the esters of the fatty acids.

TABLE V.

Ester.	K	Ester.	K
Methyl formate	2·04	Ethyl formate	2·02
Methyl acetate	2·11	Ethyl acetate	2·22
Methyl propionate	2·18	Ethyl propionate	2·24
Methyl butyrate	2·22	Propyl formate	2·11
Methyl isobutyrate . . .	2·48	Propyl acetate	2·22

With substances of simple constitution, such as liquid oxygen or nitrogen, the value of K is about 2, being rather lower than the usually accepted normal.   On the other hand, complex substances have a higher value than 2·12,[2] diphenyl-amine having $K = 2·54$, and quinoline $K = 2·43$.   The effect of complexity in structure stands out still more prominently with the optically active esters investigated by Miss Homfray and Guye.[3]

TABLE VI.

AMYL ESTERS.   K at 50–110° C.

Formate	2·13	Butyrate	2·45
Acetate	2·26	Stearate	3·34

ETHYL ESTERS.

Of	K(13–55°)	Of	K(13–55°)
Propionyl malic .	2·87 (56–107°)	Oenanthyl malic	3·12
Butyryl ,, .	3·18	Caprylyl ,, ...	3·44
Valeryl ,, .	3·40	Pelargonyl ,, ...	3·68
Caproyl ,, .	3·04	Caprinyl ,, ...	3·59

To explain these abnormally high values,[4] it might be

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[1] *Zeit. Phys. Chem.*, **15**, 101 (1894).

[2] Dutoit and Friedrich, *Arch. des Sci. Phys. et Nat.*, [4] **9**, 105 (1900).

[3] *Journ. de Chim. Phys.*, **1**, 529 (1904).

[4] It should be observed that Bogdan, *Zeit. Phys. Chem.*, **67**, 349 (1906), considers that $K = 2·1$ is not the correct value for normal liquids, which probably have higher values for K as obtained by Guye.

supposed that the substances are dissociated in the liquid state. At first sight this seems scarcely credible, since the esters in question may be distilled without decomposition, but the authors remark that the effect of the enormous internal · pressure which exists in liquids is unknown, and might lead to a rearrangement of the component parts of the molecule. It is also noteworthy that the cryoscopic and boiling-point methods give too low values for the molecular weights[1] of these compounds, and a similar result is obtained by the method of Longuinescu[2] for determining molecular weight. Another explanation of the abnormality is afforded by supposing that the molecules of complex bodies are not perfectly spherical; and then the values of MV obtained by experiment would no doubt be larger than with spherical molecules.

Also with abnormal liquids[3] the value of K rises in ascending homologous series; but here the increase for CH_2 is greater than with normal bodies, as it is chiefly due to decrease in association. The urethanes are exceptional, the higher members giving larger values for K than the lower. Generally speaking, association or the lowering in the magnitude of K may be as ascribed to the presence of certain groups containing residual affinity, such as CO, CN, OH, NH_2, and COOH.

§ 4. *SPECIFIC COHESION AND BOILING TEMPERATURE*

Walden[4] has recently found that capillarity constants may be applied in another way to estimate the degree of association of both liquids and solids. A comparison of the experimental data showed the relationship—

$$\frac{\lambda_\sigma}{a^2_\sigma} = \text{constant} = 17\cdot9 \text{ (approx.)}$$

[1] Freundler, *Ann. Chim. Phys.*, [7], 256 (1895).

[2] See p. 232.

[3] Guye and Baud, *Arch. Sci. Phys. et Nat.*, [4], 11, 449, 537 (1901).

[4] *Zeit. Phys. Chem.*, **65**, 129, 257 (1908); *Zeit. für Elektrochem.*, **14**, 713 (1908); see also Kistjakowsky, *Journ. Russ. phys. Chem. Soc.*, **84**, 70 (1902), and Dutoit and Mojoin, *Journ. Chim. Phys.*, **7**, 169 (1909).

where λ_σ is the latent heat of vaporisation at the boiling-point, and a^2_σ the specific cohesion at the same temperature. Combining this expression with Trouton's rule,[1] that the molecular heat of evaporation $(M\lambda_\sigma)$ is proportional to the absolute boiling temperature (T_σ)—

$$\frac{M\lambda_\sigma}{T_\sigma} = \text{constant} = 20\cdot7 \text{ (approx.)}$$

we have—

$$\frac{17\cdot9 M a^2_\sigma}{T_\sigma} = 20\cdot7 = \text{constant}$$

or—

$$\frac{M a^2_\sigma}{T_\sigma} = 1\cdot162 \text{ (approx.)} = K$$

We thus see that the molecular cohesion of a liquid at its boiling-point is proportional to the boiling temperature expressed on the absolute scale. The relation holds only for monomolecular liquids. The following table shows the values of K, calculated from the experimental measurements of a^2_σ and T_σ for substances of different chemical type; and it will be seen that the agreement between theory and experiment is good.

TABLE VII.

Substance.	K	x	Substance.	K	x
Stannic chloride .	1·18	0·98	Benzene . . .	1·145	1·01
Bromine . . .	1·15	1·00	Nitrobenzene .	1·132	1·02
Methyl iodide . .	1·16	1·02	Anisole . . .	1·153	1·00
Ethyl iodide . .	1·16	1·00	Naphthalene . .	1·168	0·99
Chloroform . .	1·12	1·04	Pyridine . . .	1·128	1·02
Carbon disulphide	1·13	1·02	Triethylamine .	1·173	0·98
Octane	1·13	1·02	Ethyl ether . .	1·088	1·06

Assuming the average value of K for monomolecular liquids to be 1·16, it is possible with a previous knowledge of

[1] See p. 236.

the boiling-point and specific cohesion at that temperature to calculate the molecular weight of a liquid, and, combining this with the theoretical molecular weight, the association factor (x) may be obtained—

$$\frac{M \ (\text{calc.})}{M \ (\text{theoret.})} = \frac{1 \cdot 16}{K} = x$$

The association factors of the liquids obeying the law are shown in the columns under x in the foregoing table, and it will be seen that all these liquids are unassociated at the boiling-point. Associated liquids give smaller values for K than the law demands; for example—

TABLE VIII.

Substance.	K	x	R. & S.	Substance.	K	x	R. & S.
Water . . .	0·586	1·98	2·6	Formic acid .	0·651	1·78	3·0
Methyl alcohol	0·483	2·4	3·2	Acetic acid .	0·594	1·95	2·8
Ethyl alcohol .	0·685	1·8	1·97	Acetone . .	0·913	1·27	1·26
Phenol . . .	1·02	1·13	1·18	Oxygen . .	0·840	1·38	1·17

The columns under x in the table contain the association factors for these liquids at the boiling-point calculated in the manner previously mentioned; and for comparison with these, the values of x obtained by Ramsay and Shields' method are given in the adjacent column. Walden further points out that if substances are in corresponding states at their melting-points, there should be a similar relation between the latent heat of fusion (λ_θ) and the specific cohesion (a^2_θ) at the melting-point. We should then have—

$$\frac{\lambda_\theta}{a^2_\theta} = \text{constant} = \frac{M\lambda_\theta}{Ma^2_\theta}$$

and introducing T_θ, the absolute temperature of fusion—

$$\frac{M\lambda_\theta}{T_\theta} : \frac{Ma^2_\theta}{T_\theta} = \text{constant}$$

whence it follows that—

$$\text{since } \frac{M\lambda_\theta}{T_\theta} = \text{constant}, \quad \frac{Ma^2_\theta}{T_\theta} = \text{constant (K)}$$

The experimental data confirm this relation, and the average value of K for the latter expression is found to be about $3\cdot65$ for monomolecular compounds.

TABLE IX.

Substance.	K_θ	$x = \dfrac{3\cdot65}{K_\theta}$
Chlorobenzene	$3\cdot58$	$1\cdot02$
Anisole	$3\cdot72$	$0\cdot98$
Nitrobenzene	$3\cdot75$	$0\cdot97$
Aniline	$3\cdot42$	$1\cdot07$

With associated bodies K is variable and always less than $3\cdot65$. The association factors of these substances at their melting-points may be calculated from the relation—

$$x = \frac{3\cdot65}{K}$$

and the results of this process are given with a few substances in the following table. The behaviour of the elements is worthy of special notice :—

TABLE X.

Substance.	K_θ	x	Substance.	K_θ	x
Water	$1\cdot02$	$3\cdot58$	Benzene . . .	$1\cdot97$	$1\cdot85$
Formic acid . .	$1\cdot07$	$3\cdot4$	Naphthalene . .	$2\cdot50$	$1\cdot46$
Potassium . . .	$3\cdot96$	$0\cdot9$	Bromine . . .	$1\cdot80$	$2\cdot03$
Sodium	$3\cdot30$	$1\cdot1$	Sulphur . . .	$0\cdot354$	$10\cdot3$
Tin	$3\cdot95$	$0\cdot9$	Phosphorus . .	$0\cdot50$	$6\cdot6$
Lead	$3\cdot38$	$1\cdot1$			

§ 5. *CAPILLARITY AND CONSTITUTION OF ORGANIC COMPOUNDS*

The first attempt to ascertain the influence of constitution on capillarity constants was made in 1860 by Mendelejeff.[1] He found that the molecular cohesion (a^2M) of homologues increases with additional CH_2, whilst the values of this constant for metameric substances were approximately the same. Wilhelmy,[2] however, thought the comparison of molecular cohesions unsuitable, and instead, compared the surface tensions. According to his measurements, the introduction of CH_2 does not alter the value of the coefficient, which is also the same with isomers of a similar constitution. Rodenbeck[3] determined the rise in capillary tubes of the homologous fatty acids. His results show that γ suffers a regular decrease in ascending the series. This conclusion, it will be noticed, is entirely out of harmony with those formed by Mendelejeff and Wilhelmy. Further confusion is added to the question of the capillarity relations of homologues by the work of Duclaux[4] and of Hock.[5] Both these physicists investigated the alcohols and fatty acids, but neither could find any definite relations between the homologous members. It is true that Duclaux employed the drop method which is open to suspicion, but the measurements of Hock were accurate, being made by Jäger's method, in which the pressure required to force bubbles of air from a capillary tube dipping in the liquid is measured. The results obtained by Hock are given in the adjoining table; γ_0 represents the surface tension in dynes per centimetre as obtained by interpolation from the formula—

$$\gamma_t = \gamma_0(1 - \epsilon t)$$

[1] *Compt. Rend.*, **50**, 52 ; **51**, 97 (1860).
[2] *Pogg. Ann.*, **121**, 55 (1864).
[3] *Beiblätter*, **4**, 104 (1880).
[4] *Ann. Chim. Phys.*, [5] **13**, 76 (1878).
[5] *Wien. Ber.*, **108**, [2A] 1516 (1900).

TABLE XI.

ALCOHOLS.			ACIDS.		
Substance.	γ_o	ϵ	Substance.	γ_o	ϵ
CH_3OH . .	23·97	0·00373	$H . COOH$ . .	43·63	0·00279
C_2H_5OH . .	23·63	0·00332	CH_3COOH .	27·10	0·00343
$n . C_3H_7OH$ . .	24·54	0·00294	C_2H_5COOH .	25·80	0·00310
$n . C_4H_9OH$ . .	24·32	0·00341	C_4H_9COOH .	27·62	0·00309
$C_5H_{11}OH$.	25·17	0·00287	$C_5H_{11}COOH$.	25·59	0·00313
			$C_6H_{13}COOH$.	27·23	0·00249

These results are of little value in discussing the behaviour of homologous series, owing to the disturbing influence of association which Ramsay has shown to exist in the above-mentioned compounds. Indeed, it would be surprising if any uniform behaviour could be detected in them. Rodenbeck's results, which seem to show some regularity, deal with too narrow a range of material.

The researches of Schiff[1] are distinctly in advance of those already mentioned, not on account of any greater accuracy, but because the conditions of comparison were more carefully chosen.

Schiff was the first to recognize that comparisons are not of much value unless they are made with liquids in corresponding states. This condition is attained at the critical temperature absolute, or at equal fractions thereof; but since critical constants were imperfectly known at the time, Schiff chose the boiling-point as the closest attainable approach to the comparable state. This choice was justified by the results obtained with molecular volumes at that temperature. Instead of employing γ for his comparisons, Schiff introduced the value—

$$N = \frac{\gamma}{m}$$

in which m is the molecular weight of the substance; N represents the relative number of molecules lifted along unit

[1] *Ann.*, **243**, 47 (1884); *Gazz. Chim. Ital.*, **14**, 292, 368 (1884); *Ber.*, **18**, 1603 (1885).

length of the contact line in the capillary tube. Isomeric substances were found to have almost the same values for N, the small differences between them apparently depending on the boiling-points. Some examples are given below.

TABLE XII.

Substance.	B.-P.	N×1000.	Substance.	B.-P.	N×1000.
Propyl formate .	82·5°	20·6	Propyl acetate .	102°	15·6
Methyl propionate	79·5°	20·6	Ethyl propionate .	99°	15·6
Ethyl acetate . .	75·5°	20·2	Methyl butyrate .	103°	15·9
Amyl propionate .	160·5°	8·8	Methyl isobutyrate	92°	15·7
Butyl butyrate . .	157°	8·6	Isobutyl formate .	98°	15·8
Xylene ortho . .	141°	16·0	Mesitylene . . .	165°	12·6
,, meta . .	139°	15·9	Ethyl toluene . .	162°	12·9
,, para . .	138°	15·8	Propyl benzene .	158·7°	13·0
Ethyl benzene . .	136°	16·2	Hexane. . . .	71°	16·0

The study of substitution led to the conclusion that a given atom has a constant effect on the value of N. By comparing the empirical formulæ of substances which give equal values for N, the relative values of the different elements may be calculated. For example, in the above list, hexane, the xylenes, ethyl benzene, and the isomeric esters of the formula $C_3H_{10}O_2$ have N equal to about 16. Hence—

$$C_6H_{14} = C_8H_{10} = C_5H_{10}O_2$$

and $$C = 2H \text{ and } O = 3H$$
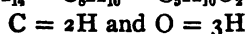
The same results for carbon and oxygen are obtained from other comparisons. The hydrogen-values of some elements were found to be as follows—

$$C = 2H \qquad Cl = 7 \text{ or } 6H$$
$$O = 3H \qquad Br = 13 \text{ or } 11H$$
$$I = 19H \qquad N = 3 \text{ or } 2H$$
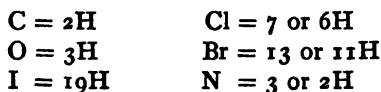
Having ascertained from these figures the hydrogen-value of a substance, it is possible to calculate N with a moderate degree of accuracy. This is done by plotting out the hydrogen values of a number of substances against the experimental values of N, and then reading off from the curve obtained the value of N corresponding to the hydrogen equivalent of the

substance in question. Schiff gives the following list from which the curve may be constructed.

TABLE XIII.

Formula.	H equivalent.	N	Formula.	H equivalent.	N
CH_4O . . .	9	59·8	C_8H_{10} . .	26	16·1
C_2H_6O . .	13	38·4	C_9H_{12} . .	30	13·1
C_3H_8O . .	17	29·0	C_9H_{18} . .	34	10·5
$C_3H_6O_2$ . .	18	27·0	$C_8H_{16}O_2$.	38	8·7
$C_4H_8O_2$ . .	22	20·4	$C_{10}H_{22}$ . .	42	7·7

These results support the conclusion which follows from the work of former observers; it seems that capillarity is almost entirely additive in character, but as can be seen from the varying values of chlorine, bromine, and nitrogen, constitutive influences are exerted, although to a restricted extent. That the constitutive side of the property remained unnoticed is almost certainly due to the inaccuracy of the methods which were at first employed, and it is only quite recently that measurements have been made with sufficient accuracy to show the effect of constitution. Feustel[1] has attacked the question by studying isomeric compounds. With the cresols, toluidines, and xylenes, he found that the ortho derivatives have the greatest surface tension, and the para the least, whilst the meta compounds are very similar to the latter.

Derivative.	CRESOLS. γ in $\frac{mg}{mm}$ at 41°	TOLUIDINES. γ in $\frac{mg}{mm}$ at 41°	XYLENES. γ in $\frac{mg}{mm}$ at 19·2°
Ortho	3·90	4·12	3·21
Meta	3·77	3·88	3·08
Para	3·74	3·76	3·03

The effect of constitution is here apparent. Linebarger[2] also has studied the effect of substitution in aromatic compounds. He showed that the introduction of a methyl group

[1] *Drude's Ann.*, **16**, 86 (1905).
[2] *Sill. Journ.*, [3] **44**, 83 (1892); *Ber.*, **25**, 937 (1892).

in the para position causes a decrease in surface tension, whilst substitution in the meta position has no influence. At the present time the constitutive nature of capillarity is unexplored, but from these results there is no doubt that future research on the subject will be profitable.

§ 6. *SPECIFIC COHESION OF FUSED METALS AND SALTS*

The specific cohesion of fused metals and salts has been investigated by Quincke in a very thorough manner. The measurements were obtained from the weight of falling drops of the liquid, or from the curvature of flat drops of the solidified material. It was found[1] that all salts and metals and some organic substances near their melting-points have specific cohesions (a^2 measured in milligrams and millimetres) which are simple multiples of the constant number 4·3. Thus—

TABLE XIV.

$a^2 = 4\cdot3.$			
Sulphur	4·3	Sodium bromide	4·1
Selenium	3·4	Potassium bromide . . .	4·5
Phosphorus	4·6	Silver bromide	4·0
Bromine	3·9	Potassium iodide	4·8

$a^2 = 8\cdot6.$					
Mercury . . .	8·6	Sodium nitrate .	8·5	Silver chloride .	8·2
Lead	8·3	Potassium nitrate .	8·3	Calcium chloride .	9·2
Silver	8·5	Lithium chloride .	8·5	Strontium chloride	8·2
Bismuth . . .	8·0	Sodium chloride .	8·4	Barium chloride .	8·3
Antimony . .	7·6	Potassium chloride	8·7		

$a^2 = 17\cdot2.$					
Platinum . .	17·8	Borax	17·3	Lithium carbonate	17·4
Cadmium . .	16·8	Glass	15·5	Sodium sulphate	17·6
Tin	16·7	Sod. am. phosphate	16·8	Potassium carbonate	14·3

$a^2 = 25\cdot8$ Palladium = 25·3 Zinc = 25·4	$a^2 = 51\cdot6$ Sodium = 53	$a^2 = 86$ Potassium = 85·7

[1] *Pogg. Ann.,* **135,** 643 (1868).

For various reasons it is probable that these relations are only apparent. In the first place, the divergence from the constant is in many cases considerable: thus $CaCl_2 = 9\cdot5$, whilst the constant is $8\cdot6$, the difference being $0\cdot9$, or about ten per cent. in excess of the observed value, and a^2 for glass is $15\cdot5$, or ten per cent. below the required value $17\cdot2$. Again, the methods of experiment, especially that of "falling drops," are not very accurate, and it may be remarked that the values obtained by other observers in other ways, whilst agreeing fairly well among themselves, are not concordant with those found by Quincke. This is especially noticeable with the specific cohesion of mercury, which varies from $6\cdot4$ found by Meyer[1] to the $8\cdot23$ of Quincke.[2] Siedentopf[3] has collected various data, and these with a few additions from other sources are shown below.

TABLE XV.

CAPILLARITY CONSTANTS OF MERCURY.

Observer.	Date.	γ	a^2
Moureau	1773	57·52	8·4
Laplace	1786	44·07	6·5
Poisson	1832	44·2	6·5
Desains	1857	45·47	6·7
Magie	1865	45·82	6·7
Sieg	1887	44·53	6·5
Michie Smith	1890	53·93	7·9
Cantor	1892	45·89	6·7
Meyer	1894	43·68	6·45
Quincke	1894	55·78	8·23
Siedentopf	1897	45·40	6·7

Siedentopf's measurements of cadmium, tin, lead, and bismuth are below contrasted with the values obtained by Quincke.

[1] Meyer, *Wied. Ann.*, **54**, 415 (1895); and Lohnstein, *Wied. Ann.*, **54**, 722 (1895).

[2] *Pogg. Ann.*, **105**, 38 (1858); and *Wied. Ann.*, **52**, 19 (1894).

[3] *Wied. Ann.*, **61**, 253 (1897).

TABLE XVI.

SPECIFIC COHESION.

Metal.	S.	Q.
Cadmium . .	21·25	17·7
Tin	17·87	17·1
Lead . . .	9·78	8·6
Bismuth . .	8·76	7·8

Under the stress of criticism, Quincke[1] somewhat modified his views, and seems to have restricted the relationship to metals. The unit chosen was then 8·5, or the specific cohesion of mercury at the melting-point. The relations between the metals then became as follows:—

$a^2 = 1 \times 8\cdot5$ Hg, Pb, Bi, and Sb
$a^2 = 2 \times 8\cdot5$ Ir, Pt, Au, Ag, Sn, Al, and Cd
$a^2 = 3 \times 8\cdot5$ Pd, Rh, Cu, Ni, Co, Fe, and Zn
$a^2 = 4 \times 8\cdot5$ K
$a^2 = 7 \times 8\cdot5$ Na

The choice of mercury as a unit is rather unfortunate, on account of the uncertainty in the value of this metal. Still further doubt is cast on the validity of Quincke's law by the recent work of Motylewski,[2] who has redetermined the values for numerous salts by the drop method. The new values for a^2 do not agree very well with those found by Quincke ; the contrast is shown in the appended table.

[1] *Wied. Ann.*, **61**, 267 (1897). See Lohnstein, *Wied. Ann.*, **53**, 1070 (1894).
[2] *Zeit. Anorgan. Chem.*, **38**, 410 (1904).

TABLE XVII.

Salt.	$\gamma \frac{mm}{m\varepsilon}$	a^2 in mm^2 Motylewski.	a^2 in mm^2 Quincke.	$\gamma(MV)^{\frac{2}{3}}$
NaCl	11·55	6·63	8·41	120·4
KCl	10·03	6·55	8·76	162·7
NaBr	10·48	4·44	4·08	112·1
KBr	9·26	4·41	4·49	136·7
NaI	9·57	3·53	—	134·3
KI	8·51	3·44	4·84	155·3
$C_2H_3O_2Na$ . .	3·95	3·11	—	63·5
KCN	9·80	8·67	—	145·9
$CaCl_2$	15·50	7·04	9·49	211·6
$BaCl_2$	17·40	4·98	8·29	268·8

§ 7. *MIXTURES* [1]

(*a*) *Non-electrolytes.*—Several different formulas have been proposed to express the relationship between the surface tension of a mixture and those of its components, but none are of general application. If the components of a mixture have the same surface tension as in the unmixed state, then, according to the co-mixture rule, the surface tension of a binary mixture would be represented by

$$\gamma = \frac{v_1\gamma_1 + v_2\gamma_2}{v_1 + v_2}$$

in which v_1 and v_2 are the volumes of the liquids, and $\gamma_1\gamma_2$ their surface tensions when unmixed. If the composition of the liquid be expressed fractionally, then ($v_1 + v_2 = 1$).

$$\gamma = v_1\gamma_1 + v_2\gamma_2$$

Further, if the liquids contract or expand on mixing, a factor, R, must be introduced, which expresses the ratio of the

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[1] The surface tension of mixtures has been examined by Duclaux, *Ann. Chim. Phys.*, [4] 21, 378 (1870) ; [5] 8, 76, (1878) ; Rodenbeck, *Beiblätter*, 4, 104 (1880) ; Volkmann, *Wied. Ann.*, 16, 321 (1882) ; Traube, *Ber.*, 17, 2294 (1884) ; *Journ. Pr. Ch.*, 31, 177 (1885) ; Ramsay and Aston, *Proc. Roy. Soc.*, 56, 182 (1894) ; Linebarger, *Sill. Journ.*, [4] 2, 226 (1896) ; Whatmough, *Zeit. Phys. Chem.*, 39, 129 (1901) ; Herzen, *Arch. des Sci. Phys. et Nat.*, [4] 14, 232 (1902) ; Drucker, *Zeit. Phys. Chem.*, 52, 678 (1905).

observed value of the density to that calculated by the admixture rule, then

$$\gamma = (v_1\gamma_1 + v_2\gamma_2)R$$

Whatmough finds that a few mixtures agree quite closely with the admixture rule in this form, the difference between the observed and calculated values for γ being about one-half per cent. The majority of the mixtures examined do not conform to the admixture rule even when this allowance for change in density is made. Generally the surface tension is less than the calculated average. In some of these abnormal mixtures the value of the surface tension lies between those of the components, and here the surface-tension–concentration curve is bent only slightly away from the admixture line. With this type of mixture it has been observed that the divergence from the normal depends on the surface tension of the components, being greater when these differ widely and less when they lie close together. There is another class of abnormal mixture in which the surface tension falls below either component, and with these the divergence from the calculated surface tension is much greater than in the former class. The following list contains some of the more important mixtures; those classed as normal obey the admixture rule either in the ordinary form or when modified to allow for changes in density.

NORMAL MIXTURES.

Ether and chloroform.

Benzene and toluene.

Ethyl and methyl iodides.

Benzene and acetone.

Chloroform and acetone.

Methylal and isobutyl acetate.

Carbon tetrachloride and chloroform.

ABNORMAL MIXTURES.

Ether and carbon disulphide.

Chloroform and benzene.

Chloroform and carbon disulphide.

Acetic acid and benzene.

Acetic acid and chloroform.

Benzene and ethyl iodide.

Ether and benzene.

Benzene and carbon disulphide.

Alcohols and water.

Fatty acids and water.

Carbon disulphide and ethylene dichloride.

It is worth noticing that Duclaux has shown that the surface-tension–concentration curves of mixtures of the alcohols and fatty acids with water take the form of a hyperbola, the surface tension may be calculated from the expression

$$\gamma = k(e^x - 1)$$

in which x is the concentration per cent. The connection.[1] between the surface tensions of mixtures and their molecular complexity is not very clear, but it is evident that in normal cases the component liquids either remain uncombined, or, if they are associated, do not break up into simpler complexes. It may be further remarked that the surface energy method shows some of the abnormal mixtures to be unassociated. With the aid of this method Ramsay and Miss Aston[2] and Pekár[3] have studied the molecular state of several mixtures. These investigators measured the rate of change in molecular surface energy with temperature and found that the value of K in many cases is normal. The data for benzene and carbon tetrachloride are shown below. The molecular weight employed in calculating $\gamma(MV)^{\frac{2}{3}}$ is the average obtained from the composition of the liquid.

TABLE XVIII.

1 molecule C_6H_6 TO 1 molecule CCl_4.

t	Density.	γ	$\gamma(MV)^{\frac{2}{3}}$	κ
16·0°	1·2597	27·70	561·9	2·33
46·2°	1·2095	23·50	492·0	2·11
78·2°	1·1596	19·71	424·5	

Normal values for K were also found with nitrobenzene–aniline,[4] toluene – piperidine, chlorobenzene – ethylene dibromide, ether–carbon disulphide, ether–benzene and ether–

[1] See Herzen, *Arch. des Sci. Phys. et Nat.*, [4] **15**, 232 (1902); and Drucker, *Zeit. Phys. Chem.*, **52**, 678 (1905).

[2] *Zeit. Phys. Chem.*, **15**, 92 (1894).

[3] *Zeit. Phys. Chem.*, **39**, 446 (1902).

[4] *Monatsheft. f. Chem.*, **28**, 831, 891 (1907).

diphenylamine. On the other hand, chloroform and carbon disulphide gave abnormal values for K.

TABLE XIX.

1 molecule $CHCl_3$ TO 1 molecule CS_2.

t	Density.	γ	$\gamma(MV)^{\frac{2}{3}}$	κ
9·0°	1·402	29·16	493·7	1·847
44·9°	1·340	24·49	427·4	2·062
61·0°	1·312	22·23	392·5	

The low value of K for the temperature interval 9–45° indicates that association takes place between these liquids; in the unmixed state both are monomolecular. Between 45° and 61° the value of K is normal, showing that the complexes decompose on raising the temperature. Mixtures of the phenols with aniline behave similarly.[1] In concluding these remarks on the surface tension of mixtures it may be mentioned that Siedentopf[2] has found that the specific cohesion of alloys of bismuth and tin at their melting-points are normal. The agreement between the experimental values of a^2 and those calculated from the admixture rule is shown in the table below.

TABLE XX.

% Bi.	a^2 (exptl.)	a^2 (calc.)
20	15·9	16·0
37·5	14·6	14·5
46·9	13·4	13·6
63·0	12·2	12·1
80·3	10·6	10·6

(*b*) *Solutions of Electrolytes.*—The surface tension of aqueous salt solutions has been very thoroughly investigated.[3] The

[1] *Monatsheft. f. Chem.*, **28**, 831, 891 (1907).

[2] *Wied. Ann.*, **61**, 260 (1897).

[3] Buliginski, *Pogg. Ann.*, **134**, 440 (1868); Valson, *Ann. Chim. Phys.*, [4] **20**, 361 (1870); Quincke, *Pogg. Ann.*, **160**, 337, 560 (1877); Volk-

addition of a salt to water increases the surface tension of the latter and the increase seems proportional to the concentration. This was first noticed by Buliginski, who also pointed out that the effect is different with different salts. Somewhat later Quincke, whilst confirming Buliginski's general conclusions, claimed that equivalent quantities of chlorides have the same effect on the surface tension of the solvent; so that for aqueous solutions of these salts the expression

$$\gamma_s = \gamma_w + 0.1783y$$

would hold where y is the number of equivalents of salt per hundred gram-molecules of water. Volkmann and others, however, have since shown that this statement is not strictly true.

The surface tension of an aqueous salt solution is best expressed by an equation of the above form which in general terms becomes—

$$\gamma_s = \gamma_w + c\mathrm{K}$$

where K is a constant varying with different salts and c is the number of gram-equivalents of the salt per litre. Surface tension is, therefore, a linear function of the concentration of the salt.

Since salt solutions thus behave normally, it is probable that the complexity of the water molecule is not altered by the addition of the salt, and this, as we shall presently see, is confirmed by the surface energy method. On the other hand, it seems that electrolytes which are themselves associated or form complex molecules with water, lower the surface tension of the latter when added to it. The fatty acids are examples of this, but sulphuric acid is exceptional, since the solutions have a greater surface tension than pure water.

Zemplén [1] has recently measured the molecular surface

mann, *Wied. Ann.*, 17, 353 (1882); Rother, *Wied. Ann.*, 21, 576 (1884); Traube, *J. pr. Ch.*, 31, 177 (1885); Sentis, *Journ. de Phys.*, [2] 6, 571 (1887); 9, 384 (1890); [3] 6, 183 (1897); Forch, *Wied. Ann.*, 68, 801 (1899); *Drud. Ann.*, 17, 744 (1905); Dorsey, *Phil. Mag.*, [5] 44, 134, 369 (1897); Sutherland, *Phil. Mag.*, [5] 40, 477 (1895); Röntgen and Schneider, *J. pr. Ch.*, 31, 192 (1885); Goldstein, *Zeit. Phys. Chem.*, 5, 233 (1891); Jäger, *Akad. Wiss. Wien.*, 100, 2A, 493 (1891).

[1] *Drud. Ann.*, 20, 783 (1906); 22, 391 (1907).

energy of aqueous salt solutions. The average molecular weight of a solution was obtained from the usual formula

$$M' = \frac{m_1 + m_2 c}{1 + c}$$

in which m_1 = molecular weight of the solvent, and m_2 and c = molecular weight and molecular concentration of the solute. If the molecular weight of water is chosen as $m_1 = x \times 18$, where x is the association factor at the temperature of measurement, it was found that the value of

$$\frac{\gamma_t (M'_t V_t)^{\frac{2}{3}} - \gamma_{t'} (M'_{t'} V_{t'})^{\frac{2}{3}}}{t - t'} = K'$$

for a salt solution is approximately equal to the normal 2·12. A still closer agreement is attained if in calculating the molecular weight of the solution allowance be made for dissociation. In this case

$$M = \frac{m_1 + m_2 c}{1 + c(1 + d)}$$

where d is the fraction of the salt dissociated, m_1 as before being calculated from $m_1 = 18x$. A few examples are given in the following table; the columns under K and K' contain

TABLE XXI.

AQUEOUS SOLUTIONS.

Salt.	Concentration per cent.	Temperature range.	Average value of K'.	Average value of K.
AgNO₃ . . .	0·074	35–94°	2·22	2·20
AgNO₃ . . .	61·56	34–91°	2·09	2·12
NaCl	5·61	35–93°	2·13	2·11
MgCl₂ . . .	21·46	10–30°	2·65	2·45
SrCl₂	8·49	10–30°	2·77	2·05
SrCl₂	22·75	10–30°	2·40	2·15
CuSO₄ . . .	6·4	10–30°	2·68	2·34
NaNO₃ . . .	20·24	10–30°	2·43	2·07
K₂CO₃ . . .	39·41	10–30°	2·38	2·20

respectively the values of the constant obtained with and without allowance for dissociation.

Zemplén claims that these results show the degree of association of water to be unaffected by the presence of a salt. It is surprising that no indication is given of " hydration " of the ions or of the formation of molecular hydrates with salts like calcium chloride and copper sulphate.

On reviewing the whole question of the surface tensions of mixtures, it seems clear that the hypothesis of varying molecular complexity does not satisfactorily explain their peculiarities, especially those of the aqueous solution of electrolytes. The thermodynamics of the problem have been developed by Gibbs,[1] by Donnan,[2] and by Lewis,[3] who have shown that the surface layers of solutions are frequently of different composition to the bulk of the liquid. Hence it would seem that even if a change in the molecular complexity of the components were to take place, the effect on the surface tension would be subordinate to that produced by the abnormal composition of the surface layers. It has been shown that if a substance lowers the surface tension of the solvent, its concentration in the surface layer is greater than in the body of the solvent; but if the surface tension is increased, the concentration at the surface is less than the average.

§ 8. *APPLICATIONS OF SURFACE ENERGY*

As we have seen, the measurement of surface energy may be employed to detect association in a liquid and also to determine the average composition of the aggregates. The method may be applied to substances of very different character—from fused metals to liquefied gases—but as yet it has not been extensively used for determining the molecular weight of dissolved substances. Pekár[4] has examined solutions

[1] *Thermodynamic Studies*, p. 321.

[2] *Zeit. Phys. Chem.*, **31**, 42 (1899) ; **46**, 197 (1903).

[3] *Phil. Mag.*, [6] **15**, 499 (1908) ; *Proc. Phys. Soc.*, **21**, 466 (1909) ; see also Freundlich, *Kapillar Chemie*, p. 57 (1909).

[4] *Zeit. Phys. Chem.*, **39**, 451 (1902).

of sulphur in carbon disulphide and in monochloride of sulphur. These solvents give normal values for K, about 2·1, hence they are unassociated. The average molecular weight of a solution of sulphur in either solvent will be given by

$$M = \frac{m + m'c}{1 + c}$$

where m is the monomolecular weight of the solvent and m' the molecular weight of the dissolved sulphur ; c expresses the number of sulphur molecules present for every one of the solvent. The surface tension of the solution is measured at different temperatures and the value of M found which satisfies .the relation

$$\frac{\gamma_t(MV)^{\frac{2}{3}} - \gamma_{t'}(MV)^{\frac{2}{3}}}{t - t'} = 2\cdot1$$

m' may then be calculated from the former equation. It will be noticed that M is assumed to be constant over the interval of temperature $t - t'$.

The results obtained by Pekár from a solution of sulphur in carbon disulphide are shown below ; the right-hand column of the table contains the values of K, which are obtained by assuming different molecular weights for the dissolved sulphur.

TABLE XXII.

	t	$\gamma(MV)^{\frac{2}{3}}$	K	K(av)
S = 32·0 . . . . $1CS_2 / 0\cdot6688S$ . . M = 58·47 . . .	17·5 60·5 99·9	43·87 37·20 30·80	1·52 1·59	1·56
$S_4 = 128\cdot2$ . . . $1CS_2 / 0\cdot1672S_4$. M = 83·59 . . .	17·5 60·5 99·9	55·68 47·22 39·11	1·93 2·02	1·98
$S_6 = 192\cdot38$ . . . $1CS_2 / 0\cdot1115S_6$. M = 87·79 . . .	17·5 60·5 99·9	57·53 48·78 40·41	1·99 2·08	2·04
$S_8 = 256\cdot5$ . . . $1CS_2 / 0\cdot0836S_8$. M = 90·04 . . .	17·5 60·5 99·9	58·51 49·61 41·10	2·02 2·12	2·07

It is clear that sulphur is associated in this solution, but the degree of association cannot be decided with certainty; it is probable that the sulphur molecule is either S_6 or S_8. Here it may be remarked that the freezing and boiling-point methods lead to the formula [1] S_8 for sulphur in this and similar solutions. The uncertainty is due to the small variation in the values of M with different degrees of polymerisation of the sulphur molecule; but the method should be more successful with substances of high molecular weight.

The temperature relations of surface energy have been applied by Schenck and Ellenberger [2] to the study of the structural change which takes place on heating certain compounds. The substances dealt with were monomolecular tautomeric liquids which may consist of two interchangeable forms. On considering the two forms, A and B, independently, it is clear that, if their critical temperatures are different, the surface-energy–temperature line of each will run parallel, as indicated by the lines AAA'A' and BBB'B' in the diagram.
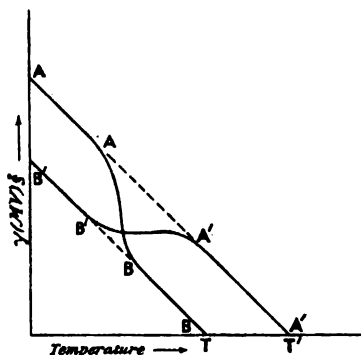

FIG. 4.

If one form, on being heated, changes into the other, then, during the temperature interval while the change is going on,

[1] Beckmann, *Zeit. Phys. Chem.*, **6**, 76 (1890); Hertz, *Zeit. Phys. Chem.*, **6**, 358 (1890); Aronstein and Meihuizen, *Akad. v. Wetensch.*, Amsterdam, **6** (1898).

[2] *Berichte*, **37**, 3443 (1904).

the figure will no longer be a straight line; but outside this temperature interval the line will preserve the linear shape belonging to either form. Thus, if form A changes into form B of lower critical temperature (T), the curve will have the shape indicated by AABB, and if form B changes into form A of higher critical temperature (T') a curve similar to B'B'A'A' will be found.

From these considerations it is evident that the surface-energy–temperature relations may be used, not only to detect tautomeric change, but also to determine the temperature limits of the stability of either form. Schenck and Ellenberger studied dibenzoylacetone, acetylacetone and acetoacetic ester. The curve obtained on heating the ketonic form of dibenzoyl-acetone :

$$C_6H_5CO.CH_2COCH_2.COC_6H_5$$
$$M.P. \ 106–110°$$
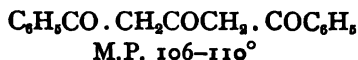
showed that the change into the enolic variety of lower critical temperature begins at 100 ° and is complete at 170°. With acetylacetone the temperature limits were not determined, but the form of the curve (as B'B'A'A') showed that the form with the lower changed to that with the higher critical temperature. It may be remarked that other physical properties indicate that heating favours the enolisation of the substance. The surface-energy–temperature curve of acetoacetic ester is linear between 16–140°, and we may conclude that no change takes place within this interval.

The critical temperature of a liquid may be obtained by calculating the temperature at which the molecular surface energy becomes zero. By employing the equation—

$$\gamma(MV)^{\frac{2}{3}} = K(T - T' - d)$$

in which T is the critical temperature, T' the temperature of measurement, and d about six degrees (see p. 23), it is possible to calculate T from a single observation. Thus, for acetyl-chloride $\gamma(MV)^{\frac{2}{3}}$ at 46·2° is 373·0 dynes, and K is about 2·04 ; hence—

$$373 = 2·04\,(T - 46·2 - 6)$$

whence $T = 235 \cdot 0°$.   Ramsay and Shields[1] have obtained the critical temperatures of several liquids in this way; a few are quoted in the adjoining list with the values obtained

Substance.	T (calc.).	T (obs.).	Substance.	T (calc.).	T (obs.).
CS_2	$280 \cdot 3°$	$272 – 280°$	C_6H_6	$288 \cdot 0°$	$288 \cdot 5°$
PCl_3	$290 \cdot 5°$	$285 \cdot 5°$	C_6H_5Cl . . .	$359 \cdot 7°$	$360 \cdot 0°$
CCl_4	$282 \cdot 1°$	$278 – 292°$	$HCOOC_2H_5$.	$214 \cdot 1°$	$214°$
$(C_2H_5)_2O$ . . .	$191 \cdot 8°$	$194 \cdot 5°$	$C_6H_5NH_2$ . .	$405°$	$425°$
C_6H_{12}	$304 \cdot 0°$	$296 \cdot 2°$	C_2H_5I	$268 \cdot 1°$	$281°$
$CH_3COOC_2H_5$.	$250 \cdot 5°$	$251 \cdot 0°$	C_2H_5SH . .	$207°$	$228°$

by direct observation.   The agreement between the two series is fairly close.

[1] *Zeit. Phys. Chem.*, **12**, 474 (1893).

CHAPTER III

VISCOSITY

§ 1. *THE FLOW OF LIQUIDS THROUGH TUBES*

THE experimental study of the rate of flow of liquids through tubes was undertaken many years before the theory of the phenomenon was understood. It seems that Dubuat,[1] in 1779, was the earliest in this field, but the results obtained by Girard[2] in 1816 were the first of any importance. Girard showed that the rate of flow through capillary tubes is proportional to the pressure on the liquid. A more complete study of the conditions governing the rate of outflow was made by Poiseuille,[3] who published his classical researches some thirty years later. Poiseuille confirmed the relation found by Girard, and, extending his researches, he was able to show that the rate of discharge varies inversely as the length of the tube, and is directly proportional to the fourth power of the diameter. The latter relation has been called "Poiseuille's law." Collecting these results, Poiseuille established the empirical relation—

$$V = K\frac{PD^4}{L}$$

in which V = volume of liquid discharged in unit time; P = pressure measured by the height of a column of mercury; D = diameter; and L = length of the tube. K represents a constant which was called the "fluidity" of the liquid.

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[1] *Principes d'hydraulique*, Paris (1779).
[2] *Memoires de l'acadamie des Sciences*, 1816.
[3] *Ann. Chim. Phys.*, [3] 7, 50 (1843); 21, 76 (1849).

Since the volume of liquid discharged is proportional to the time, T, the relation might be expressed as—

$$V = K\frac{TPD^4}{L} \quad . \quad . \quad . \quad . \quad . \quad \text{II.}$$

In the mean time the theory of moving liquids had been developed. The idea that the particles of a moving liquid do not move freely past one another seems to have been originated by Newton, but it was fully elaborated by Stokes.[1] This conception of internal friction in a liquid was first successfully applied to the flow of liquids through tubes by Hagenbach.[2]

§ 2. *COEFFICIENTS OF VISCOSITY*

The calculation of the frictional coefficient of a liquid moving through a tube is based on the conception that the particles of the liquid move parallel to the axis of the tube. Then, with the further assumption that the layer of particles next the tube-wall is motionless, and that those in the centre move the most rapidly, it may be shown that—

$$V = \frac{\pi r^4 PT}{8 \cdot L \cdot \eta} \quad . \quad . \quad . \quad . \quad . \quad \text{III.}$$

where V = volume of liquid discharged;

      P = pressure under which the discharge takes place;

      L = length of tube;

      r = radius of tube;

and η = force required to move a layer of unit area through a distance of unit length past an adjacent layer unit distance away. The value of η is called the coefficient of viscosity.

It is interesting to notice that this expression confirms that empirically deduced by Poiseuille from his experiments.

If r in Equation III. is replaced by $\frac{D}{2}$, we have—

$$V = \frac{\pi D^4 PT}{128\eta \cdot L}$$

[1] *Trans. Camb. Phil. Soc.*, **8**, 287 (1849).

[2] *Pogg. Ann.*, **109**, 385 (1860).

whence the constant K, representing Poiseuille's " Fluidity," becomes—

$$K = \frac{\pi}{128 \cdot \eta}$$

It should be observed that the expression of Hagenbach is strictly true only when certain ideal experimental conditions are observed; and of these the more important are the choice of a tube of small diameter, and the slow rate of discharge of the liquid. It is evident that when the rate of outflow assumes a finite value, the effect of pressure will not be employed entirely in overcoming friction in the tube, but a portion will be expended in imparting kinetic energy to the outflowing liquid. The error thus introduced may be corrected[1] by deducting the value of—

$$\frac{V\delta}{8\pi L} \quad (\delta = \text{density of liquid})$$

from expression III.

The viscosity of the liquid then becomes—

$$\eta = \frac{\pi r^4 PT}{8LV} - \frac{V\delta}{8\pi L} \quad . \quad . \quad . \quad . \quad \text{IV.}$$

Specific Viscosity.—In practice, the accurate measurement of all the quantities in IV. is somewhat tedious and difficult; hence it is usual to compare the time of flow of a given volume of the liquid with that of some standard, through the same tube and at the same temperature and pressure. Then, if T represents time of flow of the liquid, and T_s that of the standard liquid, we have—

$$\frac{\eta}{\eta_s} = \frac{T}{T_s}$$

where η and η_s are respectively the coefficients of viscosity of the liquid and the standard. In practice, water is usually

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[1] Hagenbach (*loc. cit.*) ; Couette, *Ann. Chim. Phys.*, [6] **21**, 433 (1890) ; Gartenmeister, *Zeit. Phys. Chem.*, **6**, 524 (1890) ; Wilberforce, *Phil. Mag.*, [5] **31**, 407 (1891).

chosen as the standard liquid, since its viscosity has been accurately measured in absolute units. The ratio η/η_* has been called the specific viscosity.[1]

Molecular Viscosity.—If Mv be the specific molecular volume of a liquid, that is the volume which contains for different substances an equal number of molecules, $(Mv)^{\frac{2}{3}}$ will represent an area over which an equal number of molecules is distributed ; it may be called the specific molecular area. Then $\eta(Mv)^{\frac{2}{3}}$ is the force required to keep a surface of specific molecular area in motion with unit velocity related to another area unit distance apart. This is called the molecular viscosity.

Molecular Viscosity Work.—The value of ηMv is equal to the molecular viscosity $\eta(Mv)^{\frac{2}{3}}$, multiplied by $(Mv)^{\frac{1}{3}}$. The latter magnitude is the cube root of the molecular volume, that is to say, it is proportional to the length of one edge of the cube, which contains for different substances an equal number of molecules ; $(Mv)^{\frac{1}{3}}$ may be called the specific molecular length. Then ηMv will represent the specific molecular work or the work required to move a surface equal to the specific molecular area through the specific molecular length at unit velocity.

The Coefficient of Viscous Traction.—Trouton[2] has recently investigated the stretching of rods made of highly viscous material. He showed that the relation between the stretching force and the rate of stretching may be expressed in the following manner[3]—

$$\frac{\mathrm{F}}{\mathrm{A}} \Big/ \frac{dv}{dx} = \lambda$$

where F = stretching force in dynes ;

　　　　A = cross-section of the rod ;

　　　　v = velocity of a given point on the rod in centimetres per second ;

　　　　x = distance of the moving point from the point of suspension.

[1] Taylor, *Proc. Edin. Roy. Soc.*, **25**, 227 (1905).

[2] *Proc. Roy. Soc.*, **77**, 426 (1906) ; *Phil. Mag.*, [6] **8**, 538 (1904).

[3] The expression is only approximately true ; for the correction which must be made, see Trouton and Rankine, *Phil. Mag.*, [6] **8**, 538 (1904).

The value of λ is constant for any given material; it is called the coefficient of viscous traction. Trouton has also shown that a simple relation exists between this coefficient and the coefficient of viscosity as measured by the outflow method; thus—

$$\eta = 3\lambda$$

The value of λ having been found, it is easy to calculate the value of η from the above equation. In this way it is possible to find the value of η for substances to which the usual methods of determining viscosity cannot be applied; the measurement of the viscosity of metals and alloys has thus been rendered possible.

§ 3. *MEASUREMENT OF VISCOSITY*

The most convenient apparatus for comparative measurements is that described by Ostwald.[1] It consists essentially of a capillary tube, *xy*, which is connected above to a bulb B, and below to a wider tube, T. The latter is bent into U-shape, and contains a bulb, A, in the lower part of its longer limb. Index marks are etched on the capillary tubing and above and below the bulb B at *n* and *m*. Since viscosity changes very rapidly with the temperature, it is important that the whole apparatus should be kept at constant temperature by immersion in a thermostat. To carry out an observation, a known volume of the liquid is introduced into the "receiving bulb" A, and sucked up the capillary tube above *n*, it is then allowed to fall and the time taken, T, for the level to pass from *n* to *m* is measured. The experiment is then repeated with the same volume of the standard liquid and the time of fall, T', is again noted.
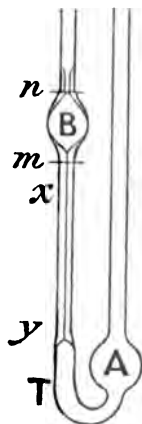
FIG. 5.

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[1] *Physico-Chemical Measurements*, p. 162.

We have seen that if the volume discharged be the same, then

$$\frac{\eta}{\eta'} = \frac{T}{T'}$$

when the pressure is constant in the two cases.

Now, in this apparatus the pressure is measured by the head of liquid, and this is of constant height, since the volume of the liquids employed is the same. Hence the pressure in either case will be proportional to the density of the liquids, and the viscosity will be obtained from the expression—

$$\frac{\eta}{\eta'} = \frac{TD}{T'D'}$$

where D and D' are the densities of the two liquids at the temperature of experiment.

It has been mentioned in § 2 that if the liquid leaves the tube with an appreciable velocity a correction must be made in the value of η as deduced from Equation IV. In this apparatus, however, if the pressure be kept low, and the dimensions of the capillary tube be suitable, the velocity of outflow is so small that no correction for this source of error is needed.

For a description of the apparatus employed in determinations of viscosity in absolute units, the reader is referred to the work of Thorpe and Rodger,[1] whose experiments represent the standard of accuracy on this subject.

§ 4. *TEMPERATURE AND VISCOSITY*

Quantitative Relations.—The earliest attempt to establish a relation between temperature and viscosity is that made by Poiseuille, who deduced from his experiments the expression—

$$\eta_t = \eta_0 / (1 + \alpha t + \beta t^2)$$

where η_t and η_0 are the coefficients of viscosity at $t°$ and $0°$ C. respectively. It was soon found that the relation is true only

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[1] Thorpe and Rodger, *Phil. Trans.*, **185A**, 397 (1894).

within narrow limits of temperature, and cannot be applied satisfactorily to all liquids. Several other empirical formulæ[1] have been advanced as satisfactorily expressing this relation, but since nearly all have been deduced from quite a small range of material they need not be mentioned.

The most comprehensive work on this subject is that of Thorpe and Rodger,[2] who, as the result of experiments with some seventy liquids, at temperatures ranging from zero to the boiling-point, concluded that Slotte's formula,[3]

$$\eta = \frac{C}{(A + t)^n}$$

is the most reliable. For liquids where the temperature coefficient is small, a contraction of this—

$$\eta = A / (1 + at + \beta t^2)$$

is quite suitable. In the table on p. 58 some of the results obtained by Thorpe and Rodger are quoted.

In columns I. and II. the values of a and β are given; in III. the temperature of experiment; in IV. and V. the calculated and observed values of $\eta \times 10^5$; and in VI. the difference between IV. and V.

On surveying this table it is evident that those substances which possess small coefficients of temperature show a very close agreement with the formula, whilst the compounds which exhibit the widest divergence have large temperature coefficients, and as a rule are known to contain molecular aggregates. Examples of the latter class are water, formic acid, and the alcohols. It is also clear that some relations exist between the magnitude of the constants and the constitution of the substance.

I. In homologous series the constants increase with rising molecular weight, but no regularity can be observed for every additional CH_2 group.

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[1] See Brillouin, *Ann. Chim. Phys.*, [8] **18**, 197 (1909).

[2] *Phil. Trans.*, **185**, 397 (1894).

[3] *Wied. Ann.*, **20**, 257, 557 (1883).

TABLE I.

Substance.	I. a	II. β	III. t	IV. $\eta \times 10^5$ calc.	V. $\eta \times 10^5$ obs.	VI. $\Delta \times 10^5$
Pentane	·01044	·0₄2301	30°	212	212	0
Hexane	·01122	·0₄3337	60	221	221	0
Heptane	·01214	·0₄4004	90	214	214	0
Octane	·01394	·0₄4926	120	208	208	0
Isopentane . . .	·01088	·0₄1331	30	204	204	0
Isohexane . . .	·01110	·0₄3509	60	207	208	1
Isoheptane . . .	·01199	·0₄3863	80	216.	216	0
Methyl iodide . .	·01067	·0₄1719	40	409	409	0
Ethyl iodide . . .	·01113	·0₄2658	70	377	378	1
Propyl iodide . .	·01278	·0₄3493	100	358	359	1
Ethyl bromide . .	·01064	·0₄1822	30	357	357	0
Propyl bromide . .	·01174	·0₄3121	70	326	327	1
Propyl chloride . .	·01104	·0₄3381	40	291	291	0
Allyl iodide . . .	·01316	·0₄3441	100	349	352	3
Allyl bromide . .	·01177	·0₄2871	70	315	316	1
Allyl chloride . .	·01111	·0₄2639	40	273	273	0
Acetone	·01064	·0₄3115	50	245	245	0
Methyl ethyl ketone	·01284	·0₄3639	80	238	239	1
Methyl propyl ketone	·01325	·0₄3965	100	238	238	0
Diethyl ketone . .	·01270	·0₄3734	100	225	226	1
o xylene	·01701	·0₄5636	140	249	254	5
m xylene	·01418	·0₄3923	130	229	233	4
p xylene	·01472	·0₄4578	130	229	233	4
Formic acid . . .	·02870	·0₃1695	100	526	542	16
Acetic acid . . .	·01826	·0₄8537	110	417	417	0
Propionic acid . .	·01720	·0₄6941	140	319	322	3
Butyric acid . . .	·02109	·0₃1107	160	315	314	− 1
Methyl alcohol . .	·01634	·0₄8371	60	354	349	−5
Allyl alcohol . .	·02552	·0₃2090	90	436	407	−29
Water	·03580	·0₃2253	100	263	283	20
Ethylene bromide .	·02007	·0₄7018	130	513	518	5
Propylene bromide .	·01924	·0₄7668	140	444	456	12
Isobutylene bromide	·02379	·0₃1256	140	489	505	16

II. Normal and iso-compounds have almost the same constants.

III. In halogen derivatives the replacement of iodine by bromine and chlorine successively causes a continuous fall in the values of the constants.

Temperatures of Comparison.—From what has been said

it will be readily acknowledged that viscosity is a property which is very strongly influenced by the physical state of the liquid, hence before the true effect of chemical structure can be discovered it is necessary to eliminate at least the chief of these physical factors : molecular aggregation and the effect of temperature. Now in many cases it is not possible completely to remove association from a liquid, and such substances must be left out of consideration. But the influence of temperature can at any rate be partially eliminated, and the question as to how this may be done is one of the chief difficulties in detecting relations between viscosity and chemical structure.

Many observers have drawn comparisons between substances at the same temperature. The results obtained from such methods are obviously inexact. Rellstab [1] was the first to attempt the solution of the difficulty. He considered that the viscosities should be compared at corresponding temperatures, that is, temperatures at which the liquids possess equal vapour pressures ; but the method did not meet with success.

By plotting out the temperature-viscosity curves of numerous substances, Thorpe and Rodger showed that the most reliable results are obtained if the viscosities are compared at temperatures where the slope of the curve is the same. This plan has the advantage that at the "temperatures of equal slope" the effect of temperature is the same for the different substances which, therefore, so far as their viscosity is concerned, should be in comparable states. It may be further shown that the ratio of the viscosities measured at two different temperatures of equal slope is constant. In thirty-three different liquids the ratio

$$\frac{\eta \text{ at slope } 0.04987}{\eta \text{ at slope } 0.04323} = 2.03 \text{ (approx.)}$$

was found to be practically the same,[2] the mean value of the ratio being 2.03, whilst the average divergence from the mean is only 1.7 per cent. It is clear that the method of

[1] *Ueber Transpiration homologer Flussigkeiten*, Bonn (1868); see Thorpe and Rodger, *Phil. Trans.*, **185**, 397 (1894).
[2] Associated liquids are exceptional.

comparison can be generally applied, and that it is independent of the value of the slope[1] at which the comparison is made. When the temperatures of equal slope are compared in homologous series, it is seen that an increment of CH_2 is accompanied by an increase in temperature; but the value is not constant for different series.

<div align="center">

TABLE II.

TEMPERATURES AT WHICH THE SLOPE IS 0·0000323.

</div>

	t	diff. for CH_2		t	diff. for CH_2
Pentane	−5·4	25·9	Methyl iodide . .	42·9	18·6
Hexane	20·5	20·6	Ethyl iodide . . .	61·5	22·1
Heptane	41·1	23·0	Propyl iodide . .	83·6	
Octane	64·1		Ethyl bromide . .	26·9	27·8
Acetone	17·8	16·3	Propyl bromide . .	54·7	
Diethyl ketone . .	50·5		Benzene	75·9	−8·1
Methyl ethyl ketone .	43·7	12·8	Toluene	67·8	10·1
Methyl propyl ketone	56·5		Ethyl benzene . .	77·9	

Associated liquids do not show this behaviour. Moreover, in all cases, with the exception of those liquids whose curves are abnormal, the ratio

$$\frac{\text{absolute temperature at slope } 0\cdot0_4323}{\text{absolute temperature at slope } 0\cdot0_4987}$$

is constant.

§ 5. *VISCOSITY AND CHEMICAL CONSTITUTION*

Historical.—We have seen in the foregoing section that the effect of temperature on viscosity is so large that if care be not taken to choose a suitable method for comparison the minor effects of constitution may be obscured. There is no doubt that this circumstance accounts for the indefinite results obtained by the earlier investigators. In 1861, Graham[2] examined the

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[1] The values of the slopes are obtained from Slotte's formula in the form—

$$d\eta/dt = nC/(A + t)^{n+1}$$

[2] *Phil. Trans.*, **151**, 373 (1861).

viscosity of a few organic liquids, and although he was only able to show that the transpiration-times of liquids increase proportionately to their boiling-points, he inferred that a connection exists between transpirability and molecular weight. Rellstab[1] took up Graham's suggestion that homologous series should be examined. To obtain comparative results he measured the time of transpiration of equivalent amounts at temperatures of equal vapour pressure. The chief deductions made from these measurements were—

1. That the transpirability of liquids increases with increasing temperature.

2. That, ascending an homologous series, the transpirability decreases[2] with every additional CH_2 group; with esters the effect of additional CH_2 is more marked in alcoholic radicle than in the acid.

3. Isomeric substances usually have different times of efflux; but the difference is less when the boiling-points of the isomers lie close to one another.

4. Substances containing a double bond have a greater transpiration-time than those of equal molecular weight with only singly linked carbon.

The work of Pribram and Handl[3] covered a much larger field than that of Rellstab or Graham. Measurement of specific viscosity at a uniform temperature enabled these investigators to frame a few general conclusions. It was observed that the specific viscosities of isomers frequently differ. An ester which contains only normal carbon chains has a greater specific viscosity than an isomeric ester which contains branched chains; also specific viscosity is increased by the substitution of halogen or a nitro group for hydrogen; and in aromatic compounds it is influenced by the nature of the substituent and its position in the molecule.

Gartenmeister[4] subsequently found that some of the generalizations put forward by Rellstab require modification.

[1] Dissertation. Bonn (1868).
[2] See also Guerout, *Compt. rend.*, 81, 1025 (1875); and 83, 1291 (1876).
[3] *Wien. Ber.*, 78, 113 (1878); 80, 17 (1879); 84, 717 (1881).
[4] *Zeit. Phys. Chem.*, 6, 524 (1890).

For example, the rule that the difference in the viscosities of isomeric esters is less the smaller the difference in their boiling-points, cannot be generally applied. But like his predecessors, Gartenmeister showed that the viscosities of the fatty acids and alcohols are abnormally great, and that as homologous series their behaviour is exceptional. He attributed the peculiarity to the presence of the hydroxyl group.

The results which we have now reviewed are quite fitted to illustrate the constitutive nature of viscosity; but the accuracy of the measurements is not sufficient to show the additive nature of the property. Moreover, it should be noted that the schemes adopted in comparing the viscosities of the different compounds were not correctly chosen. For complete illustration of the nature of viscosity we must now turn to the classical work of Thorpe and Rodger.[1]

Qualitative Relations.—The accuracy of measurement attained by these experimenters surpasses that reached by any others in this field; moreover, their method of applying the data to the study of the relations between viscosity and constitution is far in advance of any other. If the viscosity-temperature curve for any liquid is determined from a sufficient number of measurements, it is possible to obtain by interpolation the viscosity at any given temperature. The first part of the research of Thorpe and Rodger consisted of the careful construction of a number of these curves from the substances chosen for the investigation. The temperatures at which the viscosity constants of the compounds should be compared were then chosen in two ways: (A) at the boiling-point of the liquid; (B) at temperatures for which the slopes of the curves for the different substances are the same.

For each of these series of comparisons three constants were measured—

1. The absolute viscosity.
2. The molecular viscosity.
3. The molecular viscosity work.

In the following pages we shall consider only the results given by the temperatures of equal slope; those furnished by

[1] *Phil. Trans.*, **185**, 397 (1894).

the boiling-point comparison are similar but not so accurate in their quantitative relations.

B. 1. In the following table a list of the absolute viscosities of homologous series is given. The comparison is made at temperatures of equal slope 0.0_4323.

TABLE III.

Substance.	$\eta \times 10^5$	Diff.	Substance.	$\eta \times 10^5$	Diff.
Pentane	299	19	Methyl sulphide . .	335	6×2
Hexane	318	12	Ethyl sulphide . .	346	
Heptane	330	6	Acetone	329	7×2
Octane	336		Diethyl ketone . .	343	
Isopentane . . .	286	26	Methyl ethyl ketone	330	14
Isohexane	312	10	Methyl propyl ketone	344	
Isoheptane . . .	322		Formic acid . . .	373	-3
Isoprene	295	9	Acetic acid . . .	370	20
Diallyl	304		Propionic acid . .	390	-11
Methyl iodide . .	399	5	Butyric acid . . .	379	
Ethyl iodide . . .	404	3	Acetic anhydride .	378	1
Propyl iodide . .	407		Propionic anhydride	379	
Isopropyl iodide . .	390	14	Benzene	330	24
Isobutyl iodide . .	404		Toluene	354	13
Ethyl bromide . .	368	4	Ethyl benzene . .	367	
Propyl bromide .	372		Isopropyl chloride .	317	14
Isopropyl bromide .	353	7	Isobutyl chloride .	331	
Isobutyl bromide .	360		Methylene chloride .	372	5
Ethylene bromide .	455	-14	Ethylene chloride .	377	
Propylene bromide .	441				

NORMAL AND ISO COMPOUNDS.

Class.	Normal. $\eta \times 10^5$	Difference.	Iso. $\eta \times 10^5$
Pentanes	299	13	286
Hexanes	318	6	312
Heptanes	330	8	322
Propyl iodides. . .	407	17	390
Propyl bromides . .	372	19	353
Propyl chlorides . .	330	13	317

TABLE IV.

NORMAL PROPYL AND ALLYL COMPOUNDS.

Class.	*n* propyl. $\eta \times 10^5$	Diff.	Allyl. $\eta \times 10^5$
Hydrocarbons . . .	318	2×7	304
Iodides	407	1	406
Bromides	372	1	371
Chlorides	330	2	328

The curves of the alcohols did not admit of a comparison at slope $0 \cdot 0_4 323$; they were therefore compared at slope $0 \cdot 0_4 987$.

TABLE V.

	$\eta \times 10^5$	Difference.
Methyl alcohol	650	
Ethyl alcohol	606	-44
Propyl alcohol	560	-46
Butyl alcohol	575	15
Isopropyl alcohol	490	
Isobutyl alcohol	525	35
Amyl alcohol	574	
Trimethyl carbinol . . .	461	
Dimethyl ethyl carbinol . .	490	29

Inspection of these lists shows that—

1. In homologous series the effect of an additional CH_2 group is an increase in viscosity, but the value of the effect decreases as the series is ascended. The alcohols, acids, and dichlorides do not follow this rule.

2. When corresponding compounds in two simply related series are compared, the one with higher molecular weight has the greater viscosity.

3. Normal propyl compounds have larger coefficients than the corresponding allyl compounds.

4. An iso compound has a smaller coefficient than the corresponding normal compound.

5. The alcohols, acids, and dichlorides give results which differ from those furnished by the other substances.

B. 2. *Quantitative Relations.*—The above figures do not show definite quantitative relations; but a more clearly defined view of the effects of various atoms can be obtained by comparing the molecular viscosities at temperatures of equal slope. The following lists will help to make this clear.

TABLE VI.

MOLECULAR VISCOSITY × 10^4 AT SLOPE ·0,323.

Substance.	$\eta M_r^{\frac{2}{3}} \times 10^4$	Diff.	Substance.	$\eta M_r^{\frac{2}{3}} \times 10^4$	Diff.
Pentane	687	131	Isopropyl chloride .	644	116
Hexane	818	113	Isobutyl chloride .	760	
Heptane	931	104	Methylene chloride .	600	137
Octane	1035		Ethylene chloride .	737	
Isopentane . . .	663	136	Methyl sulphide . .	578	2 × 117
Isohexane . . .	799	109	Ethyl sulphide . .	812	
Isoheptane . . .	908		Acetone	572	107 × 2
Isoprene	620	108	Diethyl ketone . .	785	
Diallyl	728		Methyl ethyl ketone	671	125
Methyl iodide . .	638	140	Methyl propyl ketone	796	
Ethyl iodide . . .	778	125	Formic acid . . .	456	137
Propyl iodide . .	903		Acetic acid . . .	593	149
Isopropyl iodide .	878	132	Propionic acid . .	742	100
Isobutyl iodide . .	1010		Butyric acid . . .	842	
Ethyl bromide . .	663	111	Acetic anhydride .	838	99
Propyl bromide .	774		Propionic anhydride	1037	
Isopropyl bromide .	750	127	Benzene	688	133
Isobutyl bromide .	877		Toluene	821	118
Ethylene bromide .	973	95	Ethyl benzene . .	939	
Propylene bromide	1068		*o.* xylene	954	
Ethyl ether . . .	635		*m.* xylene	939	
Acetaldehyde . .	448		*p.* xylene	923	

The Value of CH_2—Inspection of the table shows that the effect on viscosity of addition of CH_2 is now more clearly defined than with the boiling-point comparison. The effect is very nearly the same in all the series except those of the fatty acids and aromatic hydrocarbons, and the first-named liquids are not free from the suspicion of molecular aggregation. It should be noticed that the value tends to diminish as a series is ascended. The mean effect of CH_2 is 120.

T.P.C.   F

The Value of Hydrogen.—The normal paraffins have the general formula C_nH_{2n+2}, and hence, if the effect of nCH_2 be subtracted from the values of these substances, the value of $2H$ will be obtained.

TABLE VII.

Series.	n	$n(Mv)^{\frac{2}{3}} \times 10^4 \, C_nH_{2n+2}$	nCH_2 (calc.).	H_2
Normal Paraffins .	5 6 7 8	687 818 931 1035	600 720 840 960	87 98 91 75
Iso-Paraffins . . .	5 6 7	663 799 908	579 699 819	84 100 89

Thus the mean value of $H_2 = 89$ and that of $H = 44\cdot5$ units.

The Value of Carbon.—Combining the values of H_2 and CH_2 we have $120 - 89 = 31$ for carbon.

The Influence of the Iso-grouping.—By comparing the values of a normal and iso compound it is seen that the mean value of the change of normal to iso arrangement is 21 units.

The Value of the Double Bond.—The molecular viscosity of a normal propyl compound is on an average 41 units larger than that of the corresponding allyl derivative. But in passing from the propyl to the allyl derivative $2H$ is lost, hence the complete change will be represented as follows :—

Propyl → allyl = loss of H_2 + double bond = -41

It is evident that a double bond increases the molecular viscosity by 48 units.

The Values of the Halogens may be obtained by calculating the values of the hydrocarbon residues in methyl iodide, ethyl iodide, etc., and subtracting the resulting numbers from those found in experiment with these substances. In this way iodine = 499, bromine = 372, and chlorine = 256 units.

Carbonyl Oxygen.—When the value of nCH_2 is deducted from the molecular viscosities of the aldehydes and ketones

$C_nH_{2n}CO$, the residue represents the value of carbonyl oxygen.
Thus—

Substance.	$\eta(Mv)^{\frac{1}{3}}$ (obs.) $\times 10^4$	nCH_2 (calc.).	$=O$
Acetone	572	360	212
Acetaldehyde. . . .	448	240	208
Methyl ethyl ketone .	671	480	191
Methyl propyl ketone .	796	600	196
Diethyl ketone . . .	785	600	185

Whence the mean value for carbonyl oxygen is 198.

If the fatty acids $C_nH_{2n}O''O'$ are treated in the same way, an average value of 364 is obtained, and this must represent the effect of carbonyl oxygen together with hydroxyl oxygen. Hence deducting the value of the former from 364 we obtain the effect of *hydroxylic oxygen* O' as equal to 166 units.

Applying the values of carbon, hydrogen, and carbonyl oxygen in a similar manner to the molecular viscosities of ether and acetic anhydride, we can find the value of *ethereal oxygen*; this is equal to 58 units.

These constants are collected in the following table as well as those which have been deduced in a similar manner from the molecular viscosities at a different temperature of equal slope : 0·0₄987.

TABLE VIII.

VISCOSITY CONSTANTS.

	Slope 0·0₄323.	Slope 0·0₄987.
Hydrogen	44·5	86
Carbon	31·0	60
Sulphur	246	474
Hydroxyl oxygen	166	320
Carbonyl oxygen	198	382
Ether oxygen	58	112
Chlorine (in monochlorides)	256	494
Chlorine (in dichlorides) . .	244	470
Bromine (in monobromides)	372	717
Iodine (in monoiodides) . .	499	962
Ring formation	244	465
Double bond	48	92
Iso grouping	−21	−40

It will be noticed that these figures vary according to the temperature of equal slope from which the molecular viscosities are deduced, but the ratio

$$\frac{\text{constant at slope } 0\text{·}0_4323}{\text{constant at slope } 0\text{·}0_4987}$$

is practically the same throughout the two series of measurements.

Having obtained these constants it is possible to calculate the molecular viscosity of any substance with a moderate degree of accuracy. The following list is a collection of some calculated values compared with those observed. In the third column the difference per cent. between the two values is given; it was found that the average divergence of the calculated values in about fifty compounds is only one per cent.

TABLE IX.

MOLECULAR VISCOSITY AT SLOPE 0·0₄323 × 10⁴.

Substance.	Observed.	Calculated.	Difference per cent.
Pentane . . .	687	689	−0·3
Hexane . . .	818	809	1·1
Heptane . . .	931	929	0·2
Methyl iodide .	638	664	−4·0
Ethyl iodide . .	778	784	−0·8
Methyl sulphide .	578	575	0·5
Diethyl ketone .	785	798	−1·6
Acetaldehyde .	448	438	2·2
Acetic acid . .	593	604	−1·8
Ethyl ether . .	635	627	1·3
Toluene . . .	821	814	0·8

B. 3. Turning now to the comparison of molecular viscosity work, it is easily seen that the relations are similar to those found with molecular viscosity. A list of homologues follows.

TABLE X.

Substance.	$\eta Mv \times 10^2$	Diff.	Substance.	$\eta Mv \times 10^2$	Diff.
Pentane	329	86	Methyl sulphide .	240	2×77
Hexane	415	80	Ethyl sulphide . .	393	
Heptane	495	79	Acetone	238	2×69
Octane	574		Diethyl ketone . .	376	
Isopentane . . .	320	85	Methyl ethyl ketone	302	81
Isohexane . . .	405	77	Methyl propyl ketone	383	
Isoheptane . . .	482		Formic acid . .	160	77
Methyl iodide . .	255	86	Acetic acid . . .	237	87
Ethyl iodide . .	341	84	Propionic acid . .	325	73
Propyl iodide . .	425		Butyric acid . .	397	
Ethyl bromide . .	282	71	Benzene	314	82
Propyl bromide .	353		Toluene	396	79
Isopropyl bromide	346		Ethyl benzene . .	475	

Here, again, the difference for CH_2 is fairly constant at about 80 units.

When the results are dealt with as shown for the molecular viscosities, constants can be obtained for the viscosity work of different atoms and modes of linkage, these are quoted in the following table for the temperatures of the same equal slopes as before : 0·0₄323 and 0·0₄987.

TABLE XI.

VISCOSITY WORK CONSTANTS DEDUCED FROM MOLECULAR
VISCOSITY WORK × 10².

	Slope 0·0₄323.	Slope 0·0₄987.
Hydrogen	−34	−64
Carbon	148	278
Oxygen in hydroxyl . . .	100	188
Oxygen in ether	43	73
Oxygen in carbonyl . . .	−19	−36
Sulphur	144	271
Chlorine in monochlorides .	89	167
Chlorine in dichlorides . .	82	154
Bromine in monobromides .	151	284
Iodine in monoiodides . .	218	410
Ring formation	−369	−694
Double bond	−95	−179
Iso grouping	−8	−15

We are now in a position to form some idea of the general characteristics of the viscosity of liquids.

The additive character of viscosity becomes apparent only when correct methods of comparing the quantitative measurements are adopted. This circumstance is no doubt due chiefly to the large influence which the physical states of the liquid exert on the viscosity, but also partly to the highly constitutive nature of the property. Nevertheless, when a correct comparison is made, the effects of various atoms, linkages, and replacements can be picked out with a moderate degree of accuracy, and it is possible to reconstruct the viscosity of a molecule from the viscosity effects of its component parts. Thus we have distinct evidence of the additive nature of viscosity.

Turning to the constitutive side of the property, it is evident that most of the individual atomic effects are modified to a certain extent by changes in constitution. Thus the effect of CH_2 is not strictly constant through a given homologous series, but it falls off gradually as the series is ascended. The halogen derivatives illustrate this principle most distinctly; for example, on substituting hydrogen in methane by chlorine the effect of the halogen diminishes as substitution proceeds.

TABLE XII.

At Slope 0·0₄323.

	Molecular viscosity × 10°.	Difference.	Molecular viscosity work × 10°.	Difference.
Methyl chloride . .	(420)		(135)	
Methylene dichloride	600	180	243	108
Chloroform . . .	747	147	328	85
Carbon tetrachloride	854	107	406	78

The values for methyl chloride are calculated from the atomic constants.

Before concluding these remarks on the relations between viscosity and chemical structure it is necessary to draw

attention to a series of substances which behave abnormally and do not show the regularities mentioned in the foregoing paragraphs. The compounds referred to are the alcohols; their viscosities, molecular viscosities, and molecular viscosity work at slope 0·0·987 are quoted in the following table.

TABLE XIII.

	$\eta \times 10^3$	Diff.	$\eta(Mv)^{\frac{2}{3}} \times 10^4$	Diff.	$\eta Mv \times 10^3$	Diff.
Water	—	—	390	362	105	155
Methyl alcohol . . .	650		760		260	
		−44		173		107
Ethyl alcohol . . .	606		933		367	
		−46		108		82
Propyl alcohol . . .	560		1041		449	
		15		191		121
Butyl alcohol . . .	575		1232		570	
Isopropyl alcohol . .	490		930		405	
		35		107		124
Isobutyl alcohol . .	525		1137		529	
Trimethyl carbinol . .	461		1020		480	
		29		170		47
Dimethyl ethyl carbinol	490		1190		527	

A survey of the figures shows at once that in this series there is no constant difference for each successive methylene
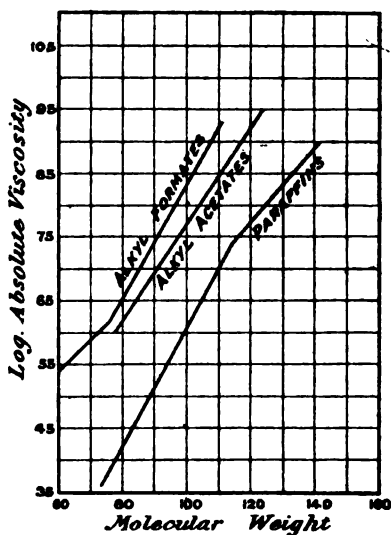
FIG. 6.

group. Moreover the molecular values of these compounds cannot be calculated with even approximate accuracy with the constants deduced from the "normal" compounds. Dunstan[1] has recently shown how the relations between molecular weight and viscosity in an homologous series can be represented graphically. If the logarithms of the absolute viscosity are plotted against those of the molecular weights (see Fig. 6) it is found that each series lies in a continuous curve; but when the curves for liquids such as the acids and alcohols are examined, this behaviour of the initial members of these series is seen to be anomalous. Now, since Ramsay and Shields[2] showed by measurements of surface tension that such substances are usually associated, the conclusion that these irregularities are due to molecular complexity is justified.

§ 6. *THE VISCOSITY OF MIXTURES OF NON-ELECTROLYTES*

Homogeneous Liquids.—The effect produced on viscosity by the formation of molecular complexes can be estimated more readily by the study of the viscosity of mixtures.

If the mixing of two liquids causes no change in the molecular condition of either, it should be possible to calculate[3] the viscosity of the mixture from the amount of each constituent present, provided that their viscosities in the pure condition be known and that neither liquid has any influence on the viscosity of the other. With such mixtures the variation in viscosity with composition would, if graphically represented, be indicated by a straight line. Now, in practice no mixture is known which attains these theoretical requirements; all those examined are found to give viscosity curves which diverge from the straight line, and their viscosities cannot be calculated from the admixture rule.

[1] *Zeit. Phys. Chem.*, **56**, 370 (1906).
[2] *Trans. Chem. Soc.*, **63**, 1101 (1893); also page 27.
[3] If the liquid contains P and Q grams of the two components *a* and *b* respectively, then the viscosity (η) of the mixture would be $= \dfrac{P\eta_a + Q\eta_b}{P + Q}$

A. E. Dunstan [1] has shown that mixtures may be classified according to the manner in which their viscosity curves diverge from the calculated line.

Class I. There are a large number of mixtures whose viscosities lie between those of the two constituents. With the

Viscosity Curves at Constant Temperature

Per cent of Constituent
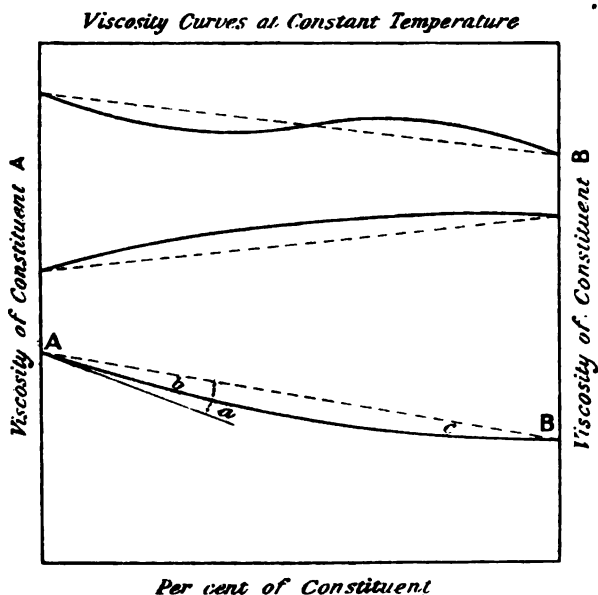
FIG. 7.

majority of these the viscosity is less than that calculated by the admixture rule, but rare instances are known where it is greater or perhaps varies from one side to the other. In cases like the latter the viscosity curve takes the form of a sinuous line intersecting the normal at some point at which the viscosity of the mixture will agree with that calculated.

The curves in Fig. 7 represent these different forms.

In this type of mixture the discrepancy between the

[1] *Trans. Chem. Soc.*, **85**, 817 (1904); **87**, 11 (1905); **91**, 83 (1907); *Proc. Chem. Soc.*, **23**, 19 (1907).

experimental and theoretical values is never very large; it seems to depend on the difference between the viscosities of the pure substances, being least in those cases where the components have nearly the same viscosity, and greatest when they differ widely. In every instance the curve takes the form of a parabola. Moreover, Dunstan points out that a relation exists between the molecular weight of a substance and the influence which it exerts on the viscosity of another compound. Thus, if a represents the angle between the tangent of the curve at A and the viscosity normal, it is found that the ratio $\dfrac{\text{mol. wt.}}{1000} \times a$ is fairly constant. For example—

TABLE XIV.

SOLUTIONS IN BENZENE.

Substance.	Molecular weight.	a	$\dfrac{M.W. \times a}{1000}$
Carbon tetrachloride.	154	52	7·9
Ethyl acetate . . .	88	94	8·27
Carbon disulphide .	76	105	7·98
Ethyl ether. . . .	74	102	7·55

If the molecular weights of the two liquids A and B are multiplied by the angles c and b respectively, the ratio of the products is constant.

TABLE XV.

Component A.	M.Wt.	c	Component B.	M.Wt.	b	$\dfrac{A \cdot c}{B \cdot b}$
Ethyl mercaptan . . .	62	13	Ethyl alcohol. . .	46	16	1·09
Carbon tetrachloride. .	154	8	Benzene	78	12	1·31
Carbon disulphide at 0°.	76	10	Methyl iodide at 0°.	142	6	0·89
Carbon disulphide at 40°	76	4	Methyl iodide at 40°	142	2	1·07
Ether	74	15	Benzene	78	12	1·18
Carbon disulphide. . .	76	3	Benzene	78	3	0·97
Ethyl acetate	88	12	Benzene	78	13	1·04

The discussion of this class of mixture may be closed with a list of the chief examples—

Ether and carbon disulphide (inflexion point).[1]
Ether and chloroform (inflexion point).[1, 2]
Ether and benzene.[3]
Ether and toluene.[3]
Carbon disulphide and benzene.[3]
Carbon disulphide and methyl iodide.[2]
Carbon disulphide and alcohol.[4]
Chloroform and benzene.[3]
Carbon tetrachloride and benzene.[2, 3]
Ethyl acetate and benzene.[3, 4]
Nitrobenzene and benzene.[3]
Acetone and alcohol.[4]
Glycol and water.[5]
Lactic acid and water.[5]

Class II. contains mixtures whose viscosity exceeds that of either constituent. As a rule, the curve assumes a characteristic shape for each mixture, there being a point of maximum viscosity which usually corresponds to definite molecular proportions. The viscosities of these mixtures often differ

TABLE XVI.

Per cent. alcohol.	Viscosity.	Per cent. alcohol.	Viscosity.
0	0·00891	55·58	0·02273
5·09	0·0101	57·51	0·02247
12·5	0·0135	60·15	0·02243
24·6	0·0185	61·06	0·02212
32·4	0·0216	65·36	0·02104
37·39	0·0229	70·54	0·01995
38·26	0·0230	73·90	0·01957
41·21	0·0232	80·20	0·01744
46·17	0·0236	100·00	0·01113
50·2	0·0233		

[1] Wijkander, *Wied. Beiblätter*, **8**, 3 (1878).
[2] Thorpe and Rodger, *Trans. Chem. Soc.*, **71**, 360 (1897).
[3] Linebarger, *Amer. Journ. Sci.*, **2**, 331 (1896).
[4] Dunstan, *Trans. Chem. Soc.*, **85**, 819 (1904).
[5] Dunstan, *Trans. Chem. Soc.*, **87**, 11 (1905).

enormously from the values calculated by the mixture rule ; for example, take the mixture of alcohol and water.

Two curves of this kind of mixture are outlined in the following figure.

Viscosity Curve at Constant Temperature
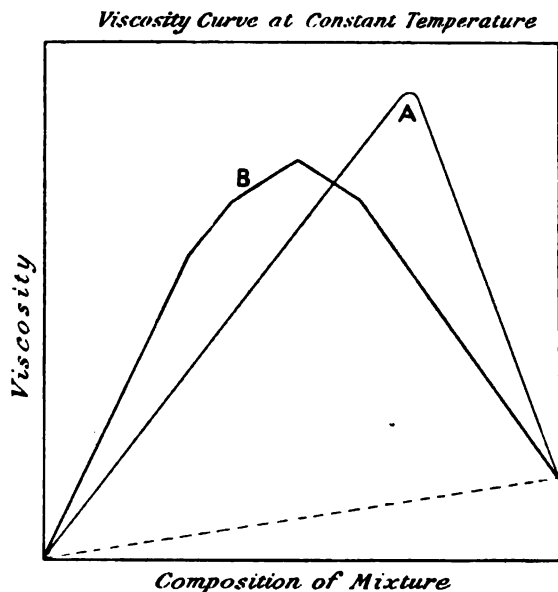
FIG. 8.—Viscosity Curve at Constant Temperature.

Curve A shows one break at the maximum point; it resembles in general outline the curve of acetic acid and water, which give the maximum viscosity at $CH_3COOH . H_2O$.

Curve B resembles the outline of that for alcohol and water : a break occurs at the maximum point which corresponds to $C_2H_5OH . 3H_2O$, whilst three others are found at the points $C_2H_5OH . 2H_2O$, $C_2H_5OH . 4–5H_2O$, and $C_2H_5OH . 6H_2O$.

A list of such mixtures is quoted in the table on p. 77.

Class III. includes mixtures which show a minimum value in their viscosity curves below that of either component; as a general rule, the curves do not diverge so widely from the

Mixture.	Composition at	
	Maximum breaks.	Subsidiary breaks.
Ethyl alcohol and water . .	C_2H_6OH .- $3H_2O$ [1, 2, 3, 4, 5]	$C_2H_6OH . 2H_2O$,[3, 4] $4-5H_2O, 6H_2O$ [3, 4]
Methyl alcohol and water [4] .	$CH_3OH . 3H_2O$ . .	$CH_3OH . 2H_2O$
Propyl alcohol and water [6] .	$C_3H_7OH . 2H_2O$ . .	——
Allyl alcohol and water [6] .	$C_3H_6OH . 3H_2O$ . .	$C_3H_6OH . 5H_2O$
Acetic acid and water [2, 7, 4] .	$CH_3COOH . H_2O$ . .	——
Pyridine and water [11] . . .	$2C_5H_6N . 5H_2O$ . .	$C_5H_6N . 5H_2O$
Sulphuric acid and water [2, 8, 9] .	$H_2SO_4 . H_2O$ . . .	$3H_2SO_4 . H_2O$
Amines and phenols [10] . .	$C_6H_5NH_2 . C_6H_5OH$	——

normal as those of the second class. A typical curve is given below.

Viscosity at Constant Temperature

Viscosity

Composition of Mixture
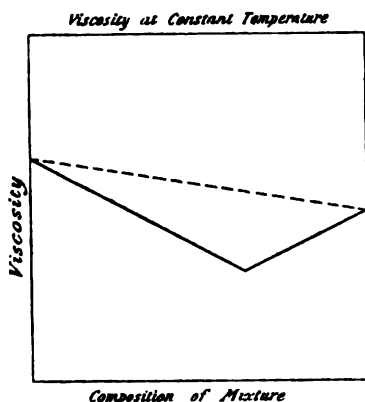
FIG. 9.—Viscosity Curve at Constant Temperature.

[1] Poiseuille, *Mem. Inst. Paris*, **9**, 433 (1846).
[2] Graham, *Phil. Trans.*, 151 (1861).
[3] Varenne and Godefroy, *Compt. Rend.*, **137**, 993 (1903).
[4] Dunstan, *Trans. Chem. Soc.*, **85**, 825 (1904).
[5] Traube, *Berichte*, **19**, 871 (1886).
[6] Dunstan, *Trans. Chem. Soc.*, **87**, 11 (1905).
[7] Wijkander, *loc. cit.*
[8] Knietsch, *Berichte*, **34**, 4069 (1901).
[9] Dunstan, *Trans. Chem. Soc.*, **91**, 84 (1907).
[10] Tsakalotos, *Bull. Soc. Chim.*, (4) **3**, 234 (1908).
[11] Dunstan, *Trans. Chem. Soc.*, **91**, 1731 (1907).

The chief mixtures of this type which have been studied are—

Mixture.	Composition at minimum break.
Benzene and acetic acid [1]	$5C_6H_6 . CH_3COOH$
Benzene and propyl alcohol [1] . .	$12C_6H_6 . C_3H_7OH$
Benzene and ethyl alcohol [1] . . .	$9C_6H_6 . C_2H_5OH$
Benzaldehyde and ethyl alcohol [1] .	$C_6H_5CHO . 5C_2H_5OH$
Benzonitrile and ethyl alcohol [2] . .	
Nitrobenzene and ethyl alcohol [2] .	
o nitrotoluene and ethyl alcohol [2] .	
m nitrotoluene and ethyl alcohol [2] .	
Aniline and nitrobenzene [2] . . .	

This varying behaviour of mixtures can be accounted for satisfactorily [4] by considering the state of molecular aggregation in the liquid.

In the second and third classes the explanation is very simple. In the third class it is seen that at least one of the components is known to be associated, and hence the fall in viscosity would be due to the breaking down of molecular aggregates into simple clusters or even single molecules. In mixtures of the second class, where the viscosity rises rapidly to high values, it may be inferred that molecular aggregation increases, and this assumption is strengthened by the fact that the viscosity reaches its highest value at a definite composition of the liquid. Moreover, the components of these mixtures are of a peculiar nature, and are known to possess a certain affinity which enables them to form molecular compounds. Other physical properties confirm this explanation; for example, in mixtures of sulphuric acid and water, the density,[5]

[1] Dunstan, *Trans. Chem. Soc.*, **85**, 817 (1904).
[2] Wagner, *Zeit. Phys. Chem.*, **46**, 872 (1903).
[3] Kremann and Ehrlich, *Monatshefte für Chemie*, **28**, 831 (1907).
[4] For another interpretation, see Jones and Veazey, *Amer. Chem. Journ.*, **37**, 405 (1907); and for criticism, Senter, *Proc. Chem. Soc.* (1910).
[5] Pickering, *Trans. Chem. Soc.*, **57**, 64, 331 (1890).

freezing point,[1] surface tension,[2] and conductivity,[3] show the formation of definite hydrates, also with alcohol and water freezing-point determinations[4] indicate the existence of the complex $C_2H_6OH . 2H_2O$.

The application of the idea to the cases in the first class is not so simple. It will be noticed that many of these mixtures are composed of inert monomolecular substances, and hence there should be no dissociation, and probably no association on mixing. If, then, change in molecular complexity were the only factor which determines the abnormal viscosity of a mixture, we should expect such liquids to obey the mixture rule. The fact that they do not obey it can only be explained by assuming either that there is some slight dissociation or association, or that there is some other influence with which we are not acquainted. For the present the former explanation seems sufficient, and perhaps it may find support in the fact that at the point of maximum divergence from the normal there is often a slight break in the curve corresponding to a definite molecular composition of the liquid.

As a general rule, a rise in temperature causes a decrease in the viscosity of a mixture; moreover, it seems that the difference between the observed and calculated values becomes less with increasing temperature. It is evident that this behaviour can be accounted for by the breaking-up of molecular complexes during the heating of the liquid. With mixtures of the second type, the large complexes are broken up, and the viscosity falls as the temperature is raised; at the same time the calculated value must fall owing to the decrease in viscosity of the pure substances, but at a much slower rate; hence the calculated and observed values of the mixture gradually approach one another. Similarly, with mixtures showing definite minima, the application of heat diminishes the molecular complexity still further, and the viscosity again

[1] Jones, *Journ. Amer. Chem. Soc.*, 16, 1 (1894); Pictet, *Compt. Rend.*, 119, 642 (1894); Burt, *Trans. Chem. Soc.*, 85, 1351 (1894).

[2] Ramsay and Shields, *Trans. Chem. Soc.*, 65, 179 (1894).

[3] Knietsch (*loc. cit.*); Pickering (*loc. cit.*).

[4] Pickering, *Trans Chem. Soc.*, 63, 1072 (1893).

falls; but the calculated value falls still more rapidly, since the unmixed liquids are more highly associated than the mixture. In this case also, the observed and theoretical values would tend to approach one another; indeed, it is quite conceivable that at a sufficiently high temperature, where the liquids are no longer associated, the two values would agree.[1]

Before considering the viscosities of solutions of electrolytes, reference must be made to the work of Arrhenius[2] on the viscosity of dilute aqueous solutions of non-electrolytes. He showed that the viscosity of a mixture can be related to the composition by the expression—

$$\eta = A^x B^y$$

Where x and y are the percentages and A and B two constants for the respective liquids. The close agreement between the observed viscosities and the values calculated[3] by this expression is shown in the following table.

TABLE XVII.

Per cent.	Substance in aqueous solution.	Specific η related to water as unity			
		At 0°.		At 25°.	
		Obs.	Calc.	Obs.	Calc.
5	Methyl alcohol .	1·159	1·155	1·114	1·112
5	Ethyl alcohol .	1·241	1·247	1·167	1·161
5	Isobutyl alcohol	1·279	1·275	1·178	1·176
2	Acetone . . .	1·111	1·118	1·103	1·095
5	Ethyl acetate .	1·067	1·063	1·044	1·044
2	Methyl acetate .	—	—	1·035	1·036
4·4	Glycerine . .	1·167	1·163	—	—
5	Ethyl ether . .	—	—	1·146	1·144
3·8	Dextrose . . .	—	—	1·153	1·162
3·8	Mannitol . . .	—	—	1·161	1·173

The value of A—the relative viscosity of a one volume

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[1] See also Beck and Treitschke, *Zeit. Phys. Chem.*, **58**, 425 (1907).

[2] *Zeit. Phys. Chem.*, 1, 288 (1887).

[3] If η be measured relative to water as unity, then $\eta = A^x$.

per cent. solution—was also calculated; the results for several liquids are given in another table.

TABLE XVIII.

A			A		
Substance.	At o°.	At 25°.	Substance.	At o°.	At 25°.
Methyl alcohol . .	1·029	1·021	Acetone	1·022	1·019
Ethyl alcohol . .	1·045	1·030	Methyl formate .	1·011	1·010
Propyl alcohol . .	1·050	1·032	Ethyl formate . .	1·019	1·015
Butyl alcohol . .	1·045	1·030	Propyl formate .	1·026	1·017
Isobutyl alcohol .	1·050	1·033	Methyl acetate . .	1·026	1·018
Isoamyl alcohol. .	1·043	1·031	Ethyl acetate . .	1·031	1·022
Trimethyl carbinol .	1·057	1·040	Propyl acetate . .	1·037	1·020
Dimethyl ethyl car-			Glycerine . . .	1·035	1·023
binol	1·059	1·040	Cane sugar . . .	1·068	1·046
Glycol	1·030	1·026	Mannitol . . .	1·051	1·043
Ethyl ether . . .	1·040	1·026	Dextrose . . .	1·044	1·040
Allyl alcohol. . .	1·041	1·026			

From these figures it is clear that many non-electrolytes increase the viscosity of water, even though they may have lower coefficients of viscosity. Some constitutional effects are also apparent, A is less with the normal than the iso alcohols, and these in turn less than the tertiary carbinols; and it will be remembered that Thorpe and Rodger formed similar conclusions.

The accuracy with which this equation expresses the viscosity of mixtures has been frequently tested.[1] Reyher[2] examined solutions of various strengths, and found that the relation does not hold for even moderately concentrated solutions; indeed, Arrhenius's own results point to this.

Reviewing the whole question, it is seen that at present the relationships between the viscosity and composition of a

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[1] Abegg, *Zeit. Phys. Chem.*, 11, 248 (1893); Lauenstein, *Zeit. Phys. Chem.*, 9, 417 (1892).

[2] Reyher, *Zeit. Phys. Chem.*, 2, 744 (1888); see, however, Fawsitt, *Proc. Roy. Soc. Edin.*, 25, 51 (1905); *Zeit. Phys. Chem.*, 48, 585 (1904); *Trans. Chem. Soc.*, 93, 1004 (1908).

mixture can be accounted for qualitatively in quite a satis-
factory manner; but an adequate quantitative expression is
still wanting, and is likely to remain so, until a more profound
knowledge of the molecular structure of liquids is attained.
From this point of view, the work of Beck[1] on isomorphous
substances is of great interest.

Isomorphous Compounds.—Dibenzyl, stilbene, azobenzene,
benzylaniline, and benzalaniline are isomorphous, and it is
remarkable that their viscosities measured at the melting-point
are almost identical, whilst that of hydrazobenzene, which is
closely allied in structure to the above substances, but not
isomorphous with them, shows a quite different viscosity.

TABLE XIX.

VISCOSITY REFERRED TO BENZENE.

Substance.	M.P.	At 5° C.	At temperature
Dibenzyl	52	2·5214	53°
Azobenzene	68	2·5078	69°
Benzalaniline	49	2·5034	50°
Stilbene	124	2·5103	125°
Benzylaniline	32	2·5106	33°
Hydrazobenzene . . .	131	2·9184	132°

When mixtures of these substances were examined, it was
found, in accordance with theory, that the melting-point
curves are always continuous : some, obeying the mixture
rule, approximate to a straight line, whilst others show a slight
minimum.   The viscosities of these mixtures were determined
at the melting-point.   The viscosity curves closely resemble
the melting-point curves ; either both are linear, or where one
shows a maximum the other shows a corresponding minimum.
The outlines of some of the curves are shown in the following
figure.

If in the latter case the measurements are made at tem-
peratures which correspond to the admixture rule, the viscosity

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[1] *Zeit. Phys. Chem.*, **48**, 652 (1904) ; also Beck, Treitschke and Ebbing-
haus, *Zeit. Phys. Chem.*, **58**, 425 (1907).

curve becomes linear. No such regularities can be observed with substances which are not isomorphous. The law has thus been established that the viscosity of isomorphous mixtures is a linear function of their composition.

Composition of Mixture
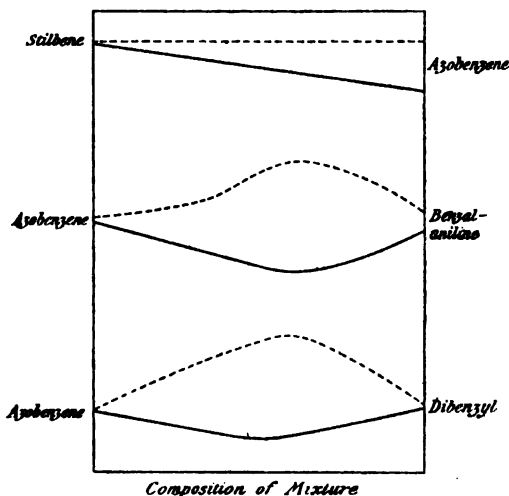
FIG. 10.—Dotted curves refer to melting-point, solid curves refer to viscosity.

§ 7. *THE VISCOSITY OF SOLUTIONS OF ELECTROLYTES*

General Relations.—On turning to solutions of electrolytes in ionising media, it is evident that besides association or combination with the solvent, the influence of ionisation will have to be taken into account. The question arises: What is the effect of ionisation on viscosity, and can any general relation be established between the two? Arrhenius[1] was the first to show that electrolytes vary in the effect which they produce on the viscosity of the solvent; some, like potassium iodide and ammonium chloride, lower the viscosity of water, whilst other salts, chiefly those containing bivalent ions, raise it. On comparing the viscosities and conductivity of normal solutions, he

[1] *Zeit. Phys. Chem.*, 1, 208 (1887).

found that those salts which exert a depressing influence [1] on the viscosity of the solvent show the greatest conductivity. Hence, it was concluded that the effect of ionisation in aqueous solution is to depress the viscosity of the solvent, but this effect may be hidden by the action of the undissociated molecules which raise the viscosity.

In the light of recent research the problem seems much more complex. In the following paragraphs it will be shown that the viscosity of a completely ionised solution depends mainly on the viscosity of the solvent, and on the size of the solvent shell round the ion. To predict the effect of ionisation on the viscosity of an unionised salt solution would be impossible without a previous knowledge of at least

(a) The molecular condition of the unionised molecules ;

(b) The diameter of the ionic "atmosphere" of solvent.

Since these magnitudes vary with different salts, it is clearly impossible to lay down a general rule for the effect of ionisation on viscosity.

Many investigations,[2] both prior and subsequent to that of Arrhenius, have been undertaken with the object of establishing relations between viscosity and the concentration of salt solutions ; but these have not met with much success since the degree of dissociation was neglected.

The solution of an electrolyte at any given temperature and concentration may be regarded 'as a mixture of two solutions—

1. A solution of undissociated molecules and molecular aggregates.

2. A solution of the ions.

If the viscosities of each of these components were known, it would be possible, assuming them to act independently, to calculate the viscosity of the given solution by the admixture

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[1] Such solutions are said to possess "negative viscosity." See Taylor, *Proc. Edin. Roy. Soc.*, **25**, 227 (1905).

[2] Sprung, *Pogg. Ann.*, **159**, 1 (1876) ; Hubner, *Pogg. Ann.*, **150**, 248 (1873) ; Slotte, *Wied. Ann.*, **20**, 257 (1883) ; *Beiblätter, Wied. Ann.*, **16**, 182 (1882) ; Brückner, *Wied. Ann.*, **42**, 287 (1891) ; Wagner, *Wied. Ann.*, **18**, 259 (1883) ; *Zeit. Phys. Chem.*, **5**, 31 (1890) ; **46**, 867 (1903).

rule; but as yet this has not been attempted. Euler,[1] however, has shown that the formula of Arrhenius may be employed to calculate the viscosity of a salt solution. It will be remembered that $\eta = A^x B^y$ for a mixture of two liquids whose coefficients of viscosity when mixed are A and B, and concentrations x and y respectively. Thus, regarding a solution of a binary electrolyte as a mixture of three liquids—

(1) Solution of undissociated salt,
(2) Solution of anion,
(3) Solution of kation,

the expression becomes—

$$\eta = S^x A^y K^z$$

where S, A, and K are the viscosities of salt, anion, and kation solutions respectively; or if a = degree of dissociation, then—

$$\eta = S^{(1-a)} A^a K^a$$

It is then clear that the viscosity of a salt solution depends on the degree of dissociation of the dissolved salt, and hence it is to be expected that some connection exists between the viscosity and conductivity of a solution. Numerous researches[2] confirm this view.

Viscosity and Conductivity.—The relations between conductivity and viscosity can be perceived by following the change of these magnitudes with varying concentration and temperature. It is found that fluidity and conductivity increase with dilution, and that the conductivity- and fluidity-concentration curves have the same form. When the temperature of a salt solution is diminished, both the conductivity and

[1] Euler, *Zeit. Phys. Chem.*, **25**, 536 (1898).
[2] G. Wiedemann, *Pogg. Ann.*, **99**, 177 (1856); *Wied. Ann.*, **20**, 537 (1883); Grotrian, *Pogg. Ann.*, **157**, 130 (1875); **160**, 238 (1887); Reyher, *Zeit. Phys. Chem.*, **2**, 744 (1888); Stephan, *Wied. Ann.*, **17**, 673 (1882); Grossmann, *Wied. Ann.*, **18**, 119 (1883); Wöllmer, *Wied. Ann.*, **52**, 347 (1894); Schlamp, *Zeit. Phys. Chem.*, **14**, 284 (1894); Pissarjewski and Lemcke, *Zeit. Phys. Chem.*, **52**, 479 (1905); Massoulier, *Compt. Rend.*, **130**, 173 (1900); **143**, 218 (1906); Kohlrausch, *Proc. Roy. Soc.*, **71**, 338 (1903); *Jahrbuch der Elektrochemie*, **8**, 156 (1901); **10**, 196 (1903); Lauenstein, *Zeit. Phys. Chem.*, **9**, 417 (1892).

fluidity decrease; moreover, the temperature curves of each resemble one another closely.   Kohlrausch showed by extrapolating the temperature-conductivity curve that the conductivity of an aqueous salt solution becomes zero at about $-35°$ C., and on treating the temperature-fluidity curve in the same way, he found that the fluidity reaches the zero point at $-34°$ C.[1]

Lauenstein has drawn attention to the fact that a given change in the constitution of an organic acid has a parallel effect on conductivity and viscosity.   Thus—

	Mol. conduct.	η
o. oxybenzoic acid . . .	0·102	1·5157
m. oxybenzoic acid. . .	0·0087	1·5787
p. oxybenzoic acid . . .	0·0028	1·7022
o. phthalic acid	0·121	1·5052
m. phthalic acid. . . .	0·028	1·4790
p. phthalic acid	0·015	1·4649

In passing from ortho to meta and para in the oxybenzoic acids, the conductivity falls whilst the viscosity rises; in the phthalic acids the conductivity and viscosity fall together.   A similar gradation is seen in bromo, chloro, and cyanobenzoic acids—

Acid.	Mol. conduct.	η
m. bromobenzoic . . .	0·0137	1·744
m. chlorobenzoic . . .	0·0155	1·713
m. cyanobenzoic . . .	0·0199	1·645

Generally speaking, conductivity and fluidity are parallel phenomena.

Viscosity and Ionic Mobility.—The study of the relation between viscosity and conductivity has shown that the latter

[1] See Hosking, *Phil. Mag.*, [6] 7, 469 (1904); and Hechler, *Drud. Ann.*, 15, 157 (1904); also Bousfield and Lowry, *Proc. Roy. Soc.*, 74, 280 (1905); Taylor and Ranken, *Proc. Edin. Roy. Soc.*, 25, 231 (1905).

depends on the internal friction of the solvent. Walden[1] examined solutions of a normal electrolyte—tetraethyl ammonium iodide—in a large number of organic solvents, and it was found that at complete dissociation—

$$\lambda_\infty \, \eta_\infty = \text{constant}$$

where λ_∞ represents the limiting value of the conductivity, and η_∞ the viscosity of the pure solvent. The following table shows in column I. the solvent, in II. the coefficient of viscosity at $0°$ C., in III. λ_∞ at $0°$ C., and in IV. the value of the constant.

TABLE XX.

AT $0°$ C.

I.	II.	III.	IV.
Solvent.	η_∞^0	λ_∞^0	$\lambda_\infty^0 \cdot \eta_\infty^0$
Acetone	0·00397	177	0·703
Propionitrile	0·00541	129	0·618
Nitromethane	0·00829	93·5	0·775
Methyl alcohol	0·00846	90	0·761
Ethyl isothiocyanate	0·00846	82	0·694
Methyl thiocyanate	0·0101	70	0·707
Acetylacetone	0·0115	57	0·656
Sym. ethyl sulphite	0·0119	55	0·655
Acetic anhydride	0·0130	52·5	0·683
Epichlorohydrine	0·0156	43·2	0·674
Ethyl alcohol	0·0179	37	0·662
Benzonitrile	0·0194	35	0·679
Furfurol	0·0248	30	0·744
Diethyl sulphate	0·0264	26	0·686
Dimethyl sulphate	0·0270	28	0·756
Nitrobenzene	0·0307	25	0·768
Benzyl cyanide	0·0338	19	0·642
Asym. ethyl sulphite . . .	0·0440	14·4	0·634
Citraconic anhydride . . .	0·0740	10·5	0·777
			0·700

At this temperature the mean value of the constant is 0·700.

[1] *Zeit. Phys. Chem.*, **55**, 244 (1906).

In the next table the values are given for 25° C.

TABLE XXA.

AT 25° C.

Solvent.	η_∞^{25}	λ_∞^{25}	$\eta_\infty^{25}\,\lambda_\infty^{25}$
Acetone	0·00316	225	0·711
Acetonitrile	0·00346	200	0·692
Acetyl chloride	0·00387	172	0·666
Propionitrile	0·00413	165	0·682
Ethyl nitrate	0·00497	138	0·686
Methyl alcohol	0·00580	124	0·719
Nitromethane	0·00619	120	0·743
Ethyl isothiocyanate	0·00618	106	0·655
Methyl thiocyanate	0·00719	96	0·690
Ethyl thiocyanate	0·00775	84·5	0·655
Acetylacetone	0·00780	82	0·640
Acetic anhydride	0·00860	76	0·654
Epichlorohydrine	0·0103	66·8	0·688
Ethyl alcohol	0·0108	60	0·648
Benzonitrile	0·0125	56·5	0·706
Benzaldehyde	0·0140	42·5 ?	(0·595)
Furfurol	0·0149	50	0·745
Diethyl sulphate	0·0160	43	0·688
Dimethyl sulphate	0·0176	43	0·757
Nitrobenzene	0·0182	40	0·728
Benzyl cyanide	0·0193	36	0·695
Lactonitrile	0·0215	(40)	(0·860)
Asym. ethyl sulphite . . .	0·0238	26·4	0·628
Ethyl cyanacetate	0·0250	28·2	0·705
Salicylic aldehyde	0·0281	25	0·703
Formamide	0·0321	? 25	0·802
Citraconic anhydride . . .	0·0338	22·5	0·760
Anisaldehyde	0·0422	16·5	0·696
Ethyl benzoylacetate . . .	0·0805	? 8	0·644
Water	0·00891	112·5	1·00

And again the mean constant, leaving out water, is almost exactly 0·700. Formamide and lactonitrile show the greatest divergence from the mean; but it is difficult to measure λ∞ with these substances, since their own conductivity is very high. Water stands by itself, but then this[1] solvent is well known to possess extreme properties.

[1] Walden and Centnerzwer, *Zeit. Phys. Chem.*, **39**, 529, 547, 580, 592, and 596 (1902).

The relation is therefore independent of temperature, and we may write—

$$\eta_\infty^t \lambda_\infty^t = \eta_\infty^{t'} \lambda_\infty^{t'} = 0\cdot700$$

or

$$\frac{\eta_\infty^t}{\eta_\infty^{t'}} = \frac{\lambda_\infty^t}{\lambda_\infty^{t'}}$$

Jones[1] and his collaborators discovered the same relation almost simultaneously with Walden. They examined the conductivity of several inorganic salts in methyl and ethyl alcohols. It was found that the conductivities of comparable solutions of binary electrolytes are inversely proportional to the viscosity of the solvent and directly proportional to the dissociation factor of the dissolved salt. Thus—

$$\frac{\lambda_v \eta}{a} = \text{constant}$$

where λ_v and η have the usual meaning and a represents the dissociation factor. Since Dutoit and Aston[2] claim to have shown that the ionising power of a solvent is proportional to its association factor (x), the above relation might also be written—

$$\frac{\lambda_v \eta}{x} = \text{constant} = C$$

or

$$\frac{\lambda_v}{C \times x} = \frac{1}{\eta} = \phi = \text{fluidity}$$

Since it was also shown that the temperature coefficients of the conductivity and fluidity are the same, it is clear that the above expression holds at all temperatures.

In this way it has been proved that for any given electrolyte in an organic solvent, the product of the viscosity and the limiting value of the conductivity is independent of the

[1] *Amer. Chem. Journ.*, **32**, 521 (1904); *Zeit. Phys. Chem.*, **56**, 162 (1906).

[2] *Compt. Rend.*, **125**, 240 (1897); see, however, Euler, *Zeit. Phys. Chem.*, **28**, 619 (1899); and Walden, *id.*, **25**, 209 (1898); **29**, 371 (1898); and **54**, 220 (1905).

nature of the solvent and temperature. This relation throws light on the state of ions in solution. The velocities of the ions must depend on the friction between them and the neighbouring particles of solvent, and it is found accordingly that the same ions move with different velocities in different solvents. But, as already explained, the temperature coefficients of the ionic velocities ($\lambda\infty$) and of the internal friction of the solvent are the same, hence it may be concluded that the friction between ions and solvent is of the same nature as that between the particles of solvent. If this be admitted, it follows that ions do not move alone in solution but are surrounded by clusters of solvent molecules, the frictional resistance to their motion being exerted between particles of the solvent.[1]

Reference may be made in this place to the work of Sutherland[2] who showed from theoretical considerations that—

$$a_v = \frac{\lambda_v \eta}{\lambda_\infty \eta_\infty}$$

where a = dissociation factor of the electrolyte at dilution v, λ_v and $\lambda\infty$ being the molecular conductivities, and η or $\eta\infty$ the viscosity of the solution and pure solvent respectively.

Carroll[3] has recently shown that the velocity with which an ion moves in solution is related to its volume and valency and to the dielectric constant and viscosity of the solvent. The relation may be shown by the expression—

$$\frac{c\eta}{n_1 E V_c^{\frac{1}{3}}} = K_c, \quad \text{and} \quad \frac{a\eta}{n_2 E V_a^{\frac{1}{3}}} = K_a$$

in which c and a = velocities of cation and anion ;

    n_1 and n_2 = valencies of cation and anion ;

    V_c and V_a = ionic volumes ;

      E and η = dielectric constant and viscosity of solvent;

K_c and K_a being constants for the two ions.

[1] *Zeit. Phys. Chem.*, **55**, 707 (1906).

[2] *Phil. Mag.*, [6] **3**, 167 (1902); also Bousfield, *Zeit. Phys. Chem.*, **53**, 257 (1905).

[3] *Amer. Chem. Journ.*, **36**, 594 (1906).

In the following tables the values of the constant for various anions and cations are given, the solvents being water and methyl alcohol. It will be seen that the numbers for the anions and cations are different, though the members of each class agree fairly well among themselves.

The mean constant for cations is 220×10^5 and that for anions is 297×10^5.

TABLE XXI.

	$H_2O.$ $\eta = 0\cdot01054$ at $18°.$[1] $E = 80\cdot8$ at $18°.$[2]			$CH_3OH.$ $\eta = 0\cdot00553$ at $25°.$[1] $E = 31\cdot7$ at $25°.$[2]	
	Ionic vol.[3]	Ionic veloc.[4]	$\kappa \times 10^5$	Ionic veloc.	$\kappa \times 10^5$
Li	11·9	33·4	191	27·8	212
Na	23·7	43·6	198	37·3	227
K	45·5	64·7	236	45·9	224
Rb	56·3	68·0	231	—	—
Cs	70·6	68·0	215	—	—
Ca	25·3	51·8	230	—	—
Sr	34·5	51·7	207	—	—
Ba	36·5	55·5	218	—	—
Cl	25·4	65·4	290	49·5	294
Br	25·6	67·6	299	50·2	297
I	25·6	66·4	294	52·4	310

The relation can be further tested by combining the equation for anion and kation, when

$$\frac{(c + a)\eta}{E\left(n_1V_c^{\frac{1}{3}} + \dfrac{K_a}{K_c}n_2V_a^{\frac{1}{3}}\right)} = \text{constant}$$

In this expression $c + a$ represents the sum of the velocities of cation and anion, and if the experimental values of $\lambda\infty$ be inserted in its place, the value of the whole expression is again found to be constant. This is illustrated by the following numbers calculated for aqueous solutions of various electrolytes.

[1] Thorpe and Rodger, *Phil. Trans.*, 185A, (1894).
[2] Drude, *Wied. Ann.*, 59, 49 (1896).
[3] Ostwald, *Lehrbuch*, I. 855 (1891).
[4] Kohlrausch, *Sitzungsber. der Konig. Preuss. Akad.*, 26, 572 (1895).

TABLE XXII.

K × 10⁵ IN AQUEOUS SOLUTION.

	Cl.	Br.	I.	− NO₃.	=SO₄.
Li	208	—	—	200	—
Na	209	219	216	201	204
K	226	230	228	215	224
Rb	222	—	—	—	—
Cs	216	—	—	—	—
Ca	219	—	—	205	218
Sr	217	—	—	202	—
Ba	216	—	—	191	—
Zn	236	—	—	—	229
Mg	226	—	—	—	205
Tl	237	237	—	224	—
Cd	220	—	—	—	213

K = 10⁵ IN CH₃OH.

NaCl at 25° . . . 227		KCl at 25° . . . 227		
NaBr ,, 25° . . . 253		KBr ,, 25° . . . 229		
NaI ,, 18° . . . 230		KI ,, 18° . . . 217		

Carroll also shows that the above relations can be derived from theory. Assuming that (1) the ion is spherical, and (2) its charge is uniformly distributed over the surface, it may be shown that—

$$v = \frac{EV^{\frac{1}{3}}}{\eta} K$$

where v = velocity of the ion. But this relation does not hold for all cases; it is approximately true when the thickness of the shell of solvent is so great in comparison with the size of the ion that the latter may be neglected. It is possible that the variations of K_c and K_a in Tables XXI. and XXII. are due to changes in the thickness of the shell of solvent enclosing the different ions.

On surveying the results of these researches it is seen that the mobility of an ion depends on the mechanical friction between the particles of solvent. Thus evidence is obtained— in agreement with that based on other physical methods [1]—

[1] See Morgan and Kanolt, *Amer. Chem. Journ.*, **28**, 572 (1902); Buchbock, *Zeit. Phys. Chem.*, **45**, 563 (1903); also specific heat, page 184.

that ions are surrounded with a shell of solvent molecules which move with them through the body of the solvent. The state of an ion in solution may be described by a quotation from Kohlrausch.[1] "About every ion moves an atmosphere of solvent whose dimensions are determined by the individual characteristics of the ion. . . . The electrical resistance of an ion is a frictional resistance which increases with the dimensions of the atmosphere. The direct action between the ion and the outer portion of the solvent diminishes as the atmosphere becomes of greater thickness."

Viscosity of Electrolytes and Constitution of the Ions.— Lauenstein[2] and Reyher had measured the viscosity of various organic acids in aqueous solution. The viscosity of the dissolved acid or salt was calculated from the viscosity of the solution from the expression $\eta = A^x B^y$. The results are quoted below; but in comparing the figures it should be

TABLE XXIII.

RELATIVE VISCOSITY (WATER = 1) AT 25° C. CALCULATED BY ARRHENIUS'S FORMULA FROM VISCOSITY OF AQUEOUS SOLUTIONS.

Substance.	η	Substance.	η
Sodium malonate	1·2277	Sodium maleate	1·2390
Sodium succinate	1·3914	Sodium citraconate . . .	1·4320
Sodium methyl malonate .	1·3965	Sodium mesaconate . . .	1·4187
Sodium methyl succinate .	1·5102	Sodium acetylene dicarbo-	
Sodium adipate	1·5447	xylate	1·7116
Sodium suberate	1·6744	Sodium malate	1·3680
Sodium azelate	1·9905	Sodium tartrate	1·3262
Sodium acetate	1·3954	Sodium cinnamate . . .	1·8107
Sodium glycollate . . .	1·3492	Sodium hydrocinnamate .	1·8685
Sodium phenylacetate . .	1·7532	Sodium benzoate . . .	1·6425
Sodium phenylglycollate .	1·7490	Sodium *o.* nitrobenzoate .	1·7040
Sodium *o.* toluylate . . .	1·8214	Sodium *m.* ,, .	1·6816
Sodium *m.* ,, . . .	1·6098	Sodium *p.* ,, .	1·4390
Sodium *p.* ,, . . .	1·7723	Sodium phthalate . . .	1·5052
Sodium *o.* oxybenzoate . .	1·5157	Sodium isophthalate . .	1·4790
Sodium *m.* ,, .	1·5787	Sodium terephthalate . .	1·4649
Sodium *p.* ,, .	1·7022	Sodium phenoxylacetate .	1·7411
Sodium fumarate	1·3371		

[1] *Proc. Roy. Soc.*, **71**, 338 (1903).
[2] *Zeit. Phys. Chem.*, **9** (1892).
[3] *Zeit. Phys. Chem.*, **2**, 744 (1888).

remembered that they are not strictly comparable, since the dissociation of the salts is unknown. The figures really show the viscosity of a mixture of undissociated salt and ions in varying proportions.

The conclusions which may be drawn from these figures are—

1. Addition of —CH_2 is accompanied by an increase of viscosity.

2. The entry of —COOH causes an increase in viscosity.

3. Loss of H_2 to form a double bond lowers the viscosity ; but a further loss of H_2 to form an acetylene bond raises it again.

4. Fumaric acid has a greater viscosity than maleic acid ; but citraconic acid is more viscous than mesaconic acid.

5. Introduction of hydroxyl lowers viscosity.

6. Isomeric benzene derivatives have different viscosities.

§ 8. *APPLICATION OF VISCOSITY RELATIONS*

Viscosity of Colloids—the change of Sol to Gel.—It is to be expected that the viscosity of a colloid would be greater than that of the corresponding crystalloid ; but no comparative measurements have been made. Kanitz[1] accounts for the abnormally high viscosity of aqueous ferric chloride by the presence of colloidal ferric hydroxide.

Von Schroeder[2] has employed viscosity in studying the change of hydrosol to hydrogel in aqueous gelatine solutions. Gelatine may be dissolved in water with the aid of heat, forming the hydrosol, but on cooling the solution to ordinary temperatures the hydrogel is gradually precipitated. By determining the viscosity of the cooled solution at intervals whilst the formation of hydrogel is going on, the rate of change of hydrosol to hydrogel can be measured. Von Schroeder found that the internal friction of a gelatine solution is not determined merely by the concentration and temperature at the time of measurement, but also by the thermal history of the

[1] *Zeit. Phys. Chem.*, **22**, 336 (1897).
[2] *Zeit. Phys. Chem.*, **45**, 75 (1903).

solution. The viscosity of a solution depends on the degree and duration of heating to which it has been previously submitted, and also on the time it has remained at the temperature of measurement. When a solution is heated the viscosity falls continuously to a constant value; but if before this constant value is reached the solution be cooled and set aside, the viscosity gradually rises again. The magnitude of the final rise depends on the duration of the preliminary heating. Thus the viscosity of a two per cent. gelatine solution which had been heated to 100° for

$$
\left.\begin{matrix} 1 \text{ hour} \\ 2 \text{ hours} \\ 6 \text{ hours} \end{matrix}\right\} \text{rose in 24 hours from} \left.\begin{matrix} 1\cdot55 \\ 1\cdot47 \\ 1\cdot28 \end{matrix}\right\} \text{to} \left.\begin{matrix} 2\cdot27 \\ 1\cdot71 \\ 1\cdot28 \end{matrix}\right\}
$$

14 hours remained constant at 1·22.

It is evident that persistent heating prevents the formation of gel.

These complicated phenomena are caused by the overlapping of two processes.

1. An irreversible change, probably a chemical reaction between the gelatine and water.

2. The reversible reaction

$$\text{Hydrosol} \xrightleftharpoons{\qquad} \text{Hydrogel}$$
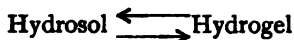
1. The speed of the first reaction was measured by heating a gelatine solution to 100° C. for varying periods. The rate of change of viscosity may be expressed by—

$$\frac{d\eta}{dt} = K(\eta - \eta_e)$$

where η_e = final value of the viscosity, and K = constant depending on the concentration of the gelatine. The reaction is therefore analogous to the hydrolysis of cane sugar; Von Schroeder called it the "saponification" reaction. It was also found that acids and bases hasten this change, whilst salts are without influence.

2. With regard to the reversible reaction, a fall in temperature favours the formation of hydrogel from hydrosol; this

reaction takes place very slowly, and it may be followed by observing the rise in viscosity of a solution after it has been heated a short time and then cooled. The formation of hydrosol is favoured by dilution and by rise in temperature. The phenomena attending the heating and cooling of gelatine solutions may be explained as follows. When the hydrogel is heated with water the hydrosol is formed ; but the latter is gradually hydrolysed, so that as the heating is continued the concentration of hydrosol becomes less. If at any moment the solution be cooled, then the change of hydrosol to hydrogel sets in ; and the amount of the latter formed will depend on the amount of hydrosol left unhydrolysed. If the solution be heated till the hydrosol is completely hydrolysed, then, on cooling, no hydrogel is formed, and the viscosity of the solution remains constant.

The formation of Complex Salts and So-called Molecular Compounds.—Viscosity may be employed to demonstrate the existence in solution of unstable compounds which cannot be isolated by the usual laboratory methods. The method of investigation will be at once apparent from what has been said of the viscosity of mixtures. If combination takes place between two substances when mixed, the viscosity of the mixture will differ widely from that calculated from the viscosities of the pure substances.

Complex Salts and Hydrates.—Kanitz[1] investigated mixtures of salts in aqueous solution, and in many cases he found distinct evidence of the formation of complex salts, the viscosity of the mixtures being greater than that calculated. In the following list, the experimental values are given (water = 1) in comparison with those obtained by calculating with Arrhenius's formula the viscosity of the mixture from the solution of each constituent.

The conclusion that complex salts are formed in these mixtures is supported by measurements of freezing-point made by Le Blanc and Noyes.[2] The data also indicate that the complexes break up on dilution.

[1] *Zeit. Phys. Chem.*, **22**, 336 (1897).
[2] *Zeit. Phys. Chem.*, **6**, 385 (1890).

TABLE XXIV.

Volume of solvent in litres.	$KNO_3+\frac{1}{2}Pb(NO_3)_2$.		$KNO_3+\frac{1}{2}Sr(NO_3)_2$.		$NaNO_3+\frac{1}{2}Pb(NO_3)_2$.		$NaNO_3+\frac{1}{2}Sr(NO_3)_2$.	
	η (obs.).	η (calc.).	η (obs.).	η (calc.).	η (obs.).	η (calc.).	η (obs.).	η (calc.).
2	1·0760	1·0233	1·0470	1·0304	1·0797	1·0688	1·0470	1·0764
4	1·0210	1·0042	1·0302	1·0107	1·0502	1·0502	1·0302	1·0365
8	1·0034	0·9986	1·0115	1·0034	1·0200	1·0145	1·0211	1·0211

The fact that mixtures of ammonium or sodium sulphate with aluminium sulphate possess a normal viscosity shows that the alums are broken up into their components when dissolved in water; and this again is confirmed by other methods of experiment.[1]

In some cases the viscosity of the mixture is less than that calculated from the components; this behaviour has been found in mixtures which contain definite complex ions. Thus a mixture of $2HCl \cdot HgCl_2$ in four litres of water has the viscosity 1·0440, whilst the calculated value is 1·0578.[2] Furthermore, it has been shown by Blanchard[3] that the viscosity of an aqueous solution of cupric chloride or nitrate is lowered by the addition of ammonia. If ammonia is added continuously, the viscosity falls until the mixture has the composition $CuX_2 \cdot 4NH_3$; further addition of ammonia raises the viscosity as in pure aqueous solution. In this way viscosity may be employed to find the composition of the complex formed.

Viscosity data concerning the formation of different hydrates are very scanty. D'Arcy[4] measured the viscosity of green and violet solutions of chrome-alum. The green solutions were made by heating the violet; and the viscosity was measured while the solution was cooling and before the reverse change of green to violet had set in. The following results were obtained :—

[1] Kistjakowsky, *Zeit. Phys. Chem.*, **6**, 119 (1890).
[2] Kanitz, *Zeit. Phys. Chem.*, **22**, 351 (1897).
[3] *Journ. Amer. Chem. Soc.*, **26**, 1315 (1904).
[4] *Phil. Mag.*, [5] **28**, 230 (1889).

η OF N $\frac{1}{10}$ SOLUTION OF CHROME-ALUM.

Temperature.	Violet solution.	Green solution.
16°	1·245	1·132
29·8	0·896	0·826
49·3	0·620	0·579
58·8	—	0·528 colour changes to green
69·4	—	0·452

(Violet solution column marked "heating" with downward arrow; Green solution column marked "cooling" with upward arrow.)

The viscosity of a green solution is less than that of a violet solution measured at the same temperature; but it is impossible to say whether this difference is due to a lower degree of hydration in the green solution, or to the presence of new complex ions.   If applied to the much discussed cases of copper and cobalt salts, the method might yield valuable evidence in support of that already furnished by other experiments.

Molecular Compounds.—These compounds might be regarded as special cases of those mentioned above, but they are considered separately, since they are formed from non-electrolytes.   Philip[1] proved from the freezing-point curves of the mixture that p. toluidine and phenol, p. toluidine and a naphthol, and a naphthylamine and phenol unite to form compounds, and these were isolated in the solid state.   Treitschke[2] has recently examined the viscosity of the fused mixtures, and has come to the same conclusion.   His results show that the compounds exist in the liquid state, but are considerably dissociated.   The decomposition of these compounds into their components can be followed by determining the viscosities of the mixtures at different temperatures.   With rising temperature, the viscosity curves of a mixture approach that calculated by the co-mixture rule from the two constants of the components.   At a sufficiently high temperature it is found that the calculated and experimental values coincide, and at this point the compound is completely dissociated.   For example, the compound $p\mathrm{CH_3 . C_6H_4NH_2 . + C_6H_5OH}$ is incapable of existing above 75°,

[1] Philip, *Trans. Chem. Soc.*, **83**, 814 (1903).

[2] *Zeit. Phys. Chem.*, **58**, 425 (1907); Kremann and Ehrlich, *Monatshefte für Chemie*, **28**, 831 (1907), have also examined aniline and *m* cresol, and sulphuric acid and water with the same results.

and that formed from α naphthylamine and phenol decomposes at 85°.

The existence of· Liquid Racemates.—The question whether liquid racemates exist has been much debated, but it is only recently [1] that viscosity data have been brought to bear on the discussion. The method consists in comparing the viscosity of an active substance with that of the inactive liquid obtained by mixing the two antipodes. It is clear that if a racemic compound is produced, the viscosity of the inactive liquid should differ from that of either isomeride.

We shall first turn to substances which are solid at the ordinary temperature, taking in order representatives of the classes of mixed crystals, pseudo-racemates, and true racemates.

Inactive Camphor oxime may be shown from the melting-point curve of mixtures of the dextro and laevo isomerides to consist of mixed crystals of these two antipodes. The following table shows the viscosity of the inactive mixture.and those of the active constituents, and since the three are the same, it is clear that the mixed crystals on fusion give a liquid mixture of the isomerides. No liquid racemate is formed.

TABLE XXV.

d. Camphor oxime, m.p. 115°.   *l.* Camphor oxime, m.p. 115°.
Viscosities referred to that of *d.* Camphor oxime at 115·8° as unity.

Mixture of	M.P.	η at 115·8°.
100 mols. *d.* oxime . . . } 0 — *l.* oxime . . . }	115·0	1·00
50 mols. *d.* oxime . . . } 50 mols. *l.* oxime . . . }	115·0	1·00
0 mols. *d.* oxime . . . } 100 mols. *l.* oxime . . . }	115·0	1·00

Inactive Carvoxime.—The melting-point of dextro or laevo

[1] Beck, *Zeit. Phys. Chem.*, 48, 670 (1904); Dunstan, *Trans. Chem. Soc.*, 93, 1815 (1908); Ranken and Taylor, *Proc. Roy. Soc. Edin.*, 27, 172 (1907).

carvoxime lies at 70·0° ; but the equi-molecular mixture melts at 93·4°. The melting-point-concentration curve shows that the inactive form of higher melting-point is a pseudo-racemate. The annexed table shows that the viscosities of mixtures of the antipodes are the same as those of either form measured at the same temperature. The inactive form breaks down on melting into a liquid mixture of the two antipodes.

TABLE XXVI.

VISCOSITIES REFERRED TO *d*. CARVOXIME AT 73° AS UNITY.

Mixture.	η	At T°.	η for pure active isomer at same temperature.
70 mols. *l*. oxime . . 30 mols. *d*. oxime . .	0·658	88·3°	0·658
50 mols. *l*. oxime . . 50 mols. *d*. oxime . .	0·521	94·4°	0·521
30 mols. *l*. oxime . . 70 mols. *d*. oxime . .	0·659	88·2°	0·659

Dimethyl Racemate and Diacetyl Racemic Ester.—The viscosity of fused dimethyl racemate is the same as that of dimethyl *d*. tartrate, and mixtures of the two substances have the same viscosity.

TABLE XXVII.

VISCOSITIES MEASURED AT 86° REFERRED TO THAT OF WATER AT 25° AS UNITY.

Mixture.	Sp. Gr.	η at 85°.	M.P.
Dimethyl *d*. tartrate	1·270	14·023	48°
95 parts active ester . . . 5 parts racemate	1·268	14·251	67°
80 parts active ester . . . 20 parts racemate	1·273	13·971	81°
50 parts active ester . . . 50 parts racemate	1·273	14·580	84°
Dimethyl racemate	1·277	14·464	85°

The small differences between the values of η seem to be due to experimental error, for there is no continuous change in viscosity on adding successively larger quantities of the inactive ester.

Methyl diacetyl racemate shows similar behaviour.

TABLE XXVIII.

VISCOSITIES MEASURED AT 104° REFERRED TO WATER AT 25° AS UNITY.

Mixture.	Sp. Gr.	η at 104°.	M.P.
Pure racemate	1·153	6·764	84°
90 parts racemate . . . $\left.\right\}$ 10 active ester	1·144	6·666	83·5°
60 parts racemate . . . . $\left.\right\}$ 40 parts active ester	1·144	6·912	90·5°
Pure active ester	1·151	6·933	103·0°

In both series it is evident that the racemate on fusion decomposes into a liquid mixture of the active forms. Dunstan has investigated a number of inactive substances which are liquids at the ordinary temperature, and he finds some indication that liquid racemates are 'capable of existence. Thus the viscosity of inactive amyl alcohol is different from that of the laevo isomeride. In the case of the two limonenes, the samples of the laevo and dextro forms examined had different viscosities, probably owing to some impurity; but the viscosity found for the inactive compound prepared from them was different from that calculated by the co-mixture rule from the values of the components.

	η		η
l. amyl alcohol	0·04476	*d.* limonene	0·00923
d. and *l.* amyl alcohol .	0·04115	*l.* limonene	0·01806
		d. and *l.* limonene (obs.) .	0·01223
		,, (calc.)	0·01365

It is, however, noteworthy that in these cases the viscosity of the racemic liquid is less than that of the active forms; if the former liquid contains complex molecules, the viscosity

might be expected to be correspondingly increased. But this circumstance may be due to association in the active liquids, and there is certainly reason to suspect this in the *l.* amyl alcohol. Further research will decide the question. It should be observed that the viscosities of racemic acid solutions seem to be slightly less than that of dextro or laevo tartaric acids.

Dunstan[1] has shown that the study of the viscosity of sodium-ammonium racemate solutions at different temperatures serves to determine the transition point of that substance; but the method has not yet been extensively applied.

The Third Isomeric Oxime of Benzaldehyde and Anisaldehyde.—Until a few years ago the oximes of benzaldehyde and anisaldehyde were known in only two isomeric forms; these, according to Hantzsch and Werner,[2] are stereoisomers, and should be represented as—

$$
\begin{array}{ccc}
\text{R . CH} & & \text{R . CH} \\
\| & \text{and} & \| \\
\text{HO . N} & & \text{N . OH} \\
\alpha \text{ or anti-oxime} & & \beta \text{ or syn-oxime}
\end{array}
$$
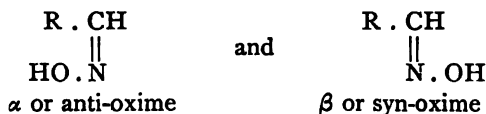
Recently a third—the α' variety—of these oximes has been brought to light.[3] This can be prepared by adding solid carbon dioxide to a strongly cooled solution of the oxime sodium salt. The α' isomerides are not very stable; when set aside at atmospheric temperatures, they change into the higher melting α form; but the latter can be reconverted to the α' isomeride by fusion and subsequent super-cooling.

The melting-points of the isomers are given in the following list:—

Oxime of	α'	α	β
Benzaldehyde . . .	16°	34·5°	126°
Anisaldehyde . . .	45°	63·5°	128°

[1] *Trans. Chem. Soc.*, **93**, 1820 (1908).

[2] *Ber.*, **23**, 11 (1890); also Stewart, *Stereochemistry* (this series).

[3] Beckmann and Lommel, *Dissertation*, Leipzig, 1902.

Beck,[1] hoping to throw some light on the nature of the low melting a' form, measured the viscosity of the three isomerides. Some of the numerical data are quoted below.

TABLE XXIX.

BENZALDOXIMES.

η measured at 126·5° C. and referred to the a' oxime as unity.

Oxime.	Sp. Gr.	η
a'	1·0245	1·000
a (anti)	1·0449	1·306
β (syn)	1·1142	1·669

ANISALDOXIMES.

η measured at 129·5° C. and referred to a' oxime as unity.

a'	1·0820	1·000
a (anti)	1·1051	1·280
β (syn)	1·1498	1·589

a OXIMES AT THE SAME TEMPERATURE.

	Benzaldoximes.	Anisaldoximes.
	η	η
a' oxime	$\left.\begin{array}{c}5\cdot462\\12\cdot477\end{array}\right\}$ at 36°	$\left.\begin{array}{c}4\cdot516\\8\cdot470\end{array}\right\}$ at 65°
a oxime		

It is evident that the syn and anti isomerides have different viscosities, and the above data further show that the viscosity of the a' modification differs from both these. From the fact that the a' and a forms are converted into one another by heating or cooling, it might be supposed that they are two polymorphic varieties of the same substance. But this cannot be the case, for the viscosity of fused monotropic forms is the same[2] under the same conditions, whilst the a and a'

[1] Beck, *Zeit. Phys. Chem.*, **48**, 674 (1904).
[2] See Beck on the viscosity of the monotropic iodine monochlorides, *Zeit. Phys. Chem.*, **48**, 678 (1904).

isomers are different when measured at the same temperature (see above table).

It seems, however, that the a' isomerides, being very unstable, are difficult to obtain free from water, and this led Beck to examine the influence of small amounts of water on the viscosity of the a oxime. It was found on adding water in increasing amount to a anisaldoxime, that the viscosity of the mixture gradually falls. Moreover, when the oxime and water are present in molecular proportions, the viscosity is the same as that obtained for the a' isomeride. This is rendered clear by the following figures.

TABLE XXX.

VISCOSITY OF a ANISALDOXIME WHEN MIXED WITH WATER.

Composition of mixture.	η at 65°.	η at $46 \cdot 5^{\circ}$.
3·13 gm. oxime + o c.c. H_2O . .	8·47	—
,, + $\frac{1}{18}$ c.c. H_2O . .	8·1	—
,, + $\frac{2}{18}$ c.c. H_2O . .	7·19	—
,, + $\frac{4}{18}$ c.c. H_2O . .	6·45	—
,, + $\frac{6}{18}$ c.c. H_2O . .	4·85	—
,, + $\frac{7}{18}$ c.c. H_2O(1 mol.)	4·60 ($a' = 4 \cdot 52$)	11·00 ($a' = 10 \cdot 93$)
,, + $\frac{8}{18}$ c.c. H_2O . .	4·19	—

Hence, we may suppose that the a' variety is simply a hydrate of the a oxime.

Moto-isomerism and Viscosity.—There are many organic compounds which occur[1] in two or more varieties of different melting-point whose existence cannot be accounted for by any of the usual hypotheses of stereoisomerism or tautomerism. Knoevenagel[2] has advanced the idea that many of these cases of isomerism are due to differences in the direction of rotation of the atoms; hence the phenomenon is called moto-isomerism.

As might be expected, the differences between moto-isomerides are very delicate; indeed, besides the melting-

[1] See Lehmann, *Molekularphysik*, Leipzig, 1888.
[2] *Berichte*, 36, 2803 (1903); 40, 508 (1907); *Annalen*, 311, 194 (1900); see also Stewart, *Stereochemistry*, p. 542.

point, no other criterion is known by which they may be distinguished. At the same time, we may remark that it still remains to be proved whether the different forms are really chemical isomerides or merely polymorphic forms of the same substance.

Knoevenagel, having discovered two varieties of *o.* nitrotoluene, pointed out [1] that the viscosity of nitrobenzene varies according to the time which has elapsed since distillation. This observation was made originally by Muhlenbein,[2] who showed that freshly distilled nitrobenzene is more viscous than a preparation which has remained undisturbed for a short period. The experimental data are as follows :—

TABLE XXXI.

Preparation.	Sp. Gr.	$\eta(H_2O = 1)$.
I. freshly distilled . . .	1·2024	2·0447
II. freshly distilled . . .	1·20180	2·0464
II. 18 hours old	—	2·0337
II. 3 months old	1·20151	2·0338

Knoevenagel considers that this shows the existence of moto-isomerides of nitrobenzene, and he further suggests that moto-isomerides in general may possess different viscosities ; if this is the case, polymorphism would be excluded.

Viscosity of Alloys.—Dunstan has studied the viscosity of lead-tin alloys. The coefficient of viscous traction was measured by Trouton's method (see page 54), and from this the value of η was calculated. The viscosity of the alloy is greater than that of either constituent, and hence there must be an increase in molecular complexity on mixing the two metals. Moreover, if the viscosity concentration curve is plotted out, a maximum point is found at the composition Sn_4Pb. This result is interesting, since a eutectic point has been found [3] for the alloy at 180°, corresponding to a mixture, 4Sn . 1Pb.

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[1] *Berichte*, **40**, 513 (1907).
[2] *Die innere Reibung von Nichtelektrolyten*, Cöthen, 1901.
[3] Roberts Austen, *Engineering*, **63**, 233 (1897).

CHAPTER IV

VOLUME RELATIONS

§ 1. *GENERAL*

THE quotient of molecular weight, divided by the weight of unit volume, expresses the volume occupied by a quantity of the substance proportional to the molecular weight—

$$V_m \text{ (molecular volume)} = \frac{\text{mol. weight}}{\text{density}}$$

We may imagine each of the atoms composing the molecule to occupy a certain definite portion of the space inhabited by the molecule as a whole. The volume occupied by each atom may be called the atomic volume. If, as Kopp and many others assumed, the sum of the atomic volumes equals the molecular volume, we may write—

$$V_m = \Sigma V_a$$

where V_a represents the volume of the atoms.

In the following pages we shall consider the volume relations of liquids and solids only; those of gases have been fully treated in another volume[1] of this series.

The general plan of investigation pursued in this subject is similar to that adopted with many other physical properties. A series of comparisons are made between pairs of substances which have the same differences in composition. In this way the volume-effects of different atoms may be obtained, and when a sufficient number have been collected the molecular

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[1] *Stoichiometry*, Young, 1908.

volume of a substance may be reconstructed from them. An estimate of the additive character of the property may be formed from the constancy of the atomic volumes deduced from different classes of compounds, or from the accuracy with which it is possible to reproduce from them the molecular volume of a substance.

It is evident that the molecular volume obtained from the quotient of molecular weight and density is only a relative measure of the space *inhabited* by the molecules. Of this space only a portion is actually occupied, the remainder is the space in which the molecules move. In the equation of van der Waals—

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

the term b represents the volume of the substance at absolute zero. Although this is not equal to the volume occupied by the actual mass of the atoms, it is proportional to the latter, and, according to van der Waals, b is four times the volume of the molecule. The ideal plan would be to compare b for different substances, but this is impossible on account of the scarcity of reliable data. But since the critical volume and critical coefficients are proportional to b, they may be used instead. It may be shown from the equation of van der Waals that the critical volume is three times b—

$$V_x = 3b$$

and that the critical coefficient or ratio of critical pressure to temperature is related to b as follows—

$$\frac{T_x}{P_x} = \frac{8b}{R}$$

in which R is the gas-constant $= \frac{PV}{273}$.

Yet another plan might be adopted in which the molecular volumes of substances are compared at " corresponding " temperatures, when their molecular volumes will bear a constant ratio to the critical volumes. These

conditions are quite easily attained in practice. Kopp, who made the first researches on this subject, was aware that in comparing molecular volumes it is of primary importance that the disturbing influence of temperature should be as far as possible excluded. He urged, therefore, that molecular volumes should be compared at temperatures of equal vapour-pressure. He adopted the boiling-point under atmospheric pressure. In this choice he was particularly fortunate, since it was afterwards found by Guldberg [1] that the boiling temperatures of different liquids are approximately equal fractions of their critical temperatures. It may be noted that other methods have been recommended. Horstmann,[2] for example, considers it better to compare molecular volumes at equal temperatures, and Tschermak,[3] Krafft,[4] and Le Bas [5] prefer to take the melting-point as a basis. If these methods be judged by the results they give, there is not much to choose between them; relations which are revealed by one are obscured by the other. As already described, the method adopted by Kopp is supported by theoretical reasons, and hence general opinion is inclined to accept it as the best. Traube [6] has laid stress on the disturbing influence of association, and he claims that this may be eliminated by determining the volume in dilute solution. This plan has the advantage of bringing solids and liquids under parallel conditions.

A few words on the experimental determination of density may not be out of place. Most measurements of the density of a liquid at the boiling-point have been made indirectly by calculation from the density at the ordinary temperature. This process requires an accurate knowledge of the boiling-point and coefficient of thermal expansion of the liquid; it is therefore somewhat tedious. Ramsay,[7] however, simplified the process by designing an apparatus for the direct measurement

[1] *Zeit. Phys. Chem.*, **5**, 374 (1890).
[2] *Ber.*, **19**, 1582 (1886); also R. Schiff, *Ann.*, **223**, 247 (1884).
[3] *Ann.*, **112**, 129; **114**, 25 (1859).
[4] *Ber.*, **15**, 1711 (1882); **17**, 1371 (1884).
[5] *Trans. Chem. Soc.*, **91**, 112 (1907).
[6] *Zeit. Anorg. Chem.*, **8**, 12 (1895).
[7] *Trans. Chem. Soc.*, **35**, 463 (1879).

of the density of the boiling liquid. With aqueous solutions, the hydrostatic method of Kohlrausch and Hallwachs[1] has given very accurate results.

§ 2. ATOMIC VOLUMES OF THE ELEMENTS

If we multiply the atomic weight by the volume of one gram of each element, we shall obtain the volume occupied by a proportionate number of atoms of the elements taken in grams. The product is called the atomic volume.

Atomic volume = atomic weight × specific volume
or atomic weight ÷ density.

This atomic volume must not be confused with that deduced from molecular volumes. With most elements the two values are different.

TABLE I.

Element.	Atomic Vol. (Kopp).	Atomic Vol. (from element).
Hydrogen	3·5	11
Carbon	11	3·4
Oxygen	12·2 or 7·8	14·3
Chlorine	22·8	22·2
Bromine	27·8	25·1
Iodine	37·5	25·6

Lothar Meyer,[2] in his study of the periodic relations between the elements, plotted out the atomic volumes against the atomic weights. The curve thus obtained runs in a series of waves which increase in amplitude as the scale of atomic weights is ascended. Broadly speaking, elements of similar chemical properties occupy corresponding positions on the waves. Borchers[3] finds that if the equivalent volumes (atomic volume ÷ maximum valency) are employed instead

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[1] *Wied. Ann.*, **53**, 14 (1894) ; **56**, 185 (1895).

[2] *Die modernen Theorien der Chemie.* The question is fully discussed by Dr. Young in *Stoichiometry*, this series, 1908.

[3] *Die Beziehungen zwischen äquivalent Volumen und Atomgewicht*, Halle, 1904.

of the atomic volumes, the curve is more regular and the relations between the elements stand out more clearly. By filling in the gaps in the curve, he ventures to predict the atomic weights and densities of unknown elements.

There is a remarkable connection between the fusibility of the elements and their position on the atomic volume curve. Volatile and easily fusible elements occur at the crests or on the rising portions of the atomic volume waves, whilst the difficultly fusible elements lie in the troughs or on the descending portions. Thus the melting-point–atomic-weight curve exhibits a similar periodicity to the atomic volume curve, but the two curves do not coincide. As a general rule, the elements within a group increase in melting-point with rising atomic weight, but the atomic volume decreases.

Also, the compressibilities of the elements are closely related to their atomic volumes. Richards[1] has found that the compressibility is a periodic function of the atomic weight, and that the structure of the compressibility curve is similar to that of the atomic volume curve. In the following table the

TABLE II.

Element.	β	At vol.	Element.	β	At vol.
Lithium . . .	8·8	13·1	Magnesium . .	2·7	13·3
Sodium . . .	15·4	23·7	Calcium . . .	5·5	25·3
Potassium . .	31·5	45·5	Zinc	1·5	9·5
Rubidium. . .	40	56	Cadmium . .	1·9	13·0
Caesium . . .	61	71	Mercury . . .	3·7	14·8
Copper . . .	0·54	7·1	Aluminium . .	1·3	10·1
Silver	0·84	10·3	Thallium . .	2·6	17·2
Gold	0·47	10·2	Phosphorus (red)	9·0	14·4
Carbon . . .	0·5	3·4	Arsenic . . .	4·3	13·3
Silicon . . .	0·16	11·4	Antimony . .	2·2	17·9
Tin	1·6	16·2	Bismuth . . .	2·8	21·2
Lead	2·2	18·2	Chlorine . . .	9·5	25·0
Sulphur . . .	12·5	15·5	Bromine . . .	51·8	25·1
Selenium . . .	11·8	18·5	Iodine . . .	13·0	25·7
Chromium . .	0·7	7·7	Manganese . .	0·7	7·7
Molybdenum. .	0·26	11·1	Iron	0·4	7·1
Palladium. . .	0·38	9·3	Nickel . . .	0·7	6·7
Platinum . . .	0·21	9·1			

compressibility (β) is expressed as the mean change in volume caused by the increase of 0·987 atmospheres pressure between 98·7 and 5 × 98·7 atmospheres.

§ 3. *THE WORK OF KOPP* [1]

Additive Relations.—Kopp was the first to undertake a systematic examination of the molecular volumes of liquids. His earlier researches were mainly occupied in collecting material and deciding the best conditions for comparison. Finally he adopted the boiling-point as the standard temperature.   In a paper published in 1855, Kopp took a general survey of the subject.   From the few data then available he deduced the rules—

(1) A constant difference in composition corresponds to a constant difference in molecular volume.

(2) Isomeric substances have the same molecular volume.

(3) The influence of one carbon atom is the same as that of two hydrogen atoms.

(4) The replacement of hydrogen by an equivalent quantity of oxygen makes but slight alteration in molecular volume.

Some of the data on which these generalizations were based are quoted in the list on p. 112.

Kopp proceeded to calculate the atomic volume of the elements.   It was found that addition of CH_2 to a compound causes an increase in molecular volume of about 22 units. Combining this with the fact that C is equal in volume-effect to H_2, it follows that $C = 11$ and $H = 5\cdot5$.   From these values the volume-effects of other elements were obtained.   Oxygen was found to vary according as it was situated within the radicle, as in the acetyl of acetic acid, or without the radicle, as in a substance like alcohol—

$$\left.\begin{array}{c} C_2H_3O \\ H \end{array}\right\}O \qquad\qquad \left.\begin{array}{c} C_2H_5 \\ H \end{array}\right\}O$$
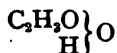
Acetic acid   Alcohol

[1] *Pogg. Ann.*, **47**, 113 (1839); **52**, 243, 262 (1844); *Ann.*, **41**, 79 (1842); **96**, 153, 303 (1855); **250**, 1 (1889).

Thus, in modern terminology, carbonyl oxygen and hydroxylic oxygen have respectively the values

$$O'' = 12 \cdot 2 \quad \text{and} \quad O' = 7 \cdot 8$$

Similarly for sulphur—

$$S'' = 28 \cdot 6 \quad \text{and} \quad S' = 22 \cdot 6$$

and chlorine, bromine and iodine—

$$Cl = 22 \cdot 8; \ Br = 27 \cdot 8; \ I = 37 \cdot 5$$

TABLE III.

MOLECULAR VOLUME AT THE BOILING-POINT.

Substance.	Formula.	Calculated.	Observed.
Benzene	C_6H_6	99·0	96·0–99·7
Naphthalene	$C_{10}H_8$	154·0	149·2
Acetaldehyde. . . .	C_2H_4O	56·2	56·0–56·9
Acetone	C_3H_6O	78·2	77·3–77·6
Methyl alcohol . . .	CH_4O	40·8	41·9–42·2
Ethyl alcohol. . . .	C_2H_6O	62·8	61·8–62·5
Amyl alcohol. . . .	$C_5H_{12}O$	128·8	123·6–124·4
Formic acid	CH_2O_2	42·0	40·9–41·8
Acetic acid	$C_2H_4O_2$	64·0	63·5–63·8
Propionic acid . . .	$C_3H_6O_2$	86·0	85·4
Butyric acid	$C_4H_8O_2$	108·0	106·4–107·8
Valerianic acid . . .	$C_5H_{10}O_2$	130·0	130·2–131·2
Ethyl ether	$C_4H_{10}O$	106·8	105·6–106·4
Methyl formate . . .	$C_2H_4O_2$	64·0	63·4
Methyl acetate . . .	$C_3H_6O_2$	86·0	83·7–85·8

Kopp further showed that the molecular volume of a substance can be calculated from the sum of the volumes of the component atoms with approximate accuracy.

For example—

$$\text{Acetic Acid} \qquad C_2H_4O''O'$$

$$2C = 22$$
$$4H = 22$$
$$O'' = 12 \cdot 2$$
$$O' = \underline{7 \cdot 8}$$
$$64 \cdot 0 \text{(calc.)} \qquad 63 \cdot 5\text{–}63 \cdot 8 \text{(obs.)}$$

A glance at the foregoing table will show that the conformity between the observed and calculated volumes is generally close, and this led Kopp to infer that the molecular volume of a liquid is approximately equal to the sum of the atomic volumes.

Whilst later research has shown that Kopp laid undue emphasis on the additive features of this property, it must not be supposed that he entirely denied the influence of constitution. Indeed, the fact that he attributed different values to oxygen and sulphur when within or without the radicle clearly showed that he recognized the possibility of constitutive influences. He also observed that the rule of equality in the volume of isomerides holds only if the substances have similar constitution.

These investigations excited general interest, and in the three following decades numerous researches were undertaken to submit Kopp's generalizations to further test. Almost every fresh research made clearer the constitutive nature of the property, while the scope of the additive laws was correspondingly narrowed.

§ 4. *CONSTITUTIVE RELATIONS*

It is scarcely profitable to consider the enormous mass of detail which may be adduced to show the influence of chemical constitution, and therefore attention may be restricted to a few of the chief modifications of structure.

Homologues.—When measured at the boiling-point the molecular volumes of a homologous series do not increase regularly for each additional CH_2 group. The increment becomes larger as the series is ascended, but in most cases the homologous increment lies between 21 and 24 units. For illustration of this rule the accompanying data may be consulted ; they are collected from the researches of Gartenmeister,[1] Pinette,[2] and Dobriner.[3]

[1] *Ann.*, **233**, 249 (1886).
[2] *Ann.*, **243**, 32 (1888).
[3] *Ann.*, **243**, 11 (1888) ; see also Elsässer, *Ann.*, **218**, 337 (1883) ; Zander, *Ann.*, **225**, 74 (1884).

<div align="center">TABLE IV.</div>

<div align="center">NORMAL ALKYL IODIDES.</div>

Substance.	Formula.	V_m at B.P.	Δ
Methyl iodide	CH_3I	64·1	
Ethyl iodide	C_2H_5I	85·7	21·6
Propyl iodide	C_3H_7I	106·8	21·1
Butyl iodide	C_4H_9I	128·5	21·7
Amyl iodide	$C_5H_{11}I$	151·2	22·7
Hexyl iodide	$C_6H_{13}I$	175·5	24·3
Heptyl iodide	$C_7H_{15}I$	198·6	23·1

<div align="center">NORMAL ALKYL ETHERS.</div>

Methyl ethyl ether . .	C_3H_8O	84·0	
Diethyl ether	$C_4H_{10}O$	106·1	22·1
Ethyl propyl ether . .	$C_5H_{12}O$	127·8	21·7
Ethyl butyl ether . .	$C_6H_{14}O$	150·1	22·3
Ethyl heptyl ether . .	$C_9H_{20}O$	220·8	3 × 23·6
Ethyl octyl ether . . .	$C_{10}H_{22}O$	246·7	25·9

<div align="center">ALKYL ESTERS OF FORMIC ACID.</div>

Methyl formate . . .	$C_2H_4O_2$	62·7	
Ethyl formate	$C_3H_6O_2$	84·6	21·9
Propyl formate . . .	$C_4H_8O_2$	106·2	21·6
Butyl formate	$C_5H_{10}O_2$	127·6	21·4
Amyl formate	$C_6H_{12}O_2$	150·5	22·9
Hexyl formate	$C_7H_{14}O_2$	173·3	22·8
Heptyl formate	$C_8H_{16}O_2$	196·7	23·4
Octyl formate	$C_9H_{18}O_2$	220·3	23·6

<div align="center">ALKYL ESTERS OF VALERIANIC ACID.</div>

Methyl ester	$C_6H_{12}O_2$	149·1	
Ethyl ester	$C_7H_{14}O_2$	174·5	25·4
Propyl ester	$C_8H_{16}O_2$	197·8	23·3
Butyl ester	$C_9H_{18}O_2$	222·1	24·3
Amyl ester	$C_{10}H_{20}O_2$	245·8	23·7
Hexyl ester	$C_{11}H_{22}O_2$	272·0	26·2
Heptyl ester	$C_{12}H_{24}O_2$	297·4	25·4
Octyl ester	$C_{13}H_{26}O_2$	322·6	25·2

Gartenmeister thought that the successive increase in the volume of CH_2 was approximately constant in any given series, and Lossen[1] made use of this in an attempt to express the

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[1] *Ann.*, **254**, 42 (1889).

molecular volume of a member of an homologous series by a formula. With the esters of fatty acids, the lowest term in the series—methyl formate—has $V_m = 62 \cdot 7$; and the difference between this and the next term—methyl acetate—is 20·5.

Assuming the successive increase of the CH_2 value to be 0·5 units, we may write for any member of the series $C_nH_{2n}O_2$.

$$V_m = 62 \cdot 7 + (n - 2)\, 20 \cdot 5 + 0 \cdot 5\, \frac{(n - 2)^2}{2}$$

According to Kopp, $V_{H_2} = V_0$, and this combined with the assumption that the average initial difference for CH_2 is 20·9, enabled Lossen to calculate from—

$$V_{C_2H_4O}(\text{Methyl formate}) = 62 \cdot 7$$

that

$$V_C = 10 \cdot 45 V_H = 5 \cdot 225 V_0 = 10 \cdot 45$$

Then the above equation becomes—

$$V_m = 10 \cdot 45n + 5 \cdot 225m + 10 \cdot 45o + 0 \cdot 25(n - 2)^2$$

where n, m, and o are respectively the numbers of atoms of carbon, hydrogen, and oxygen. The formula may be applied to several classes of saturated fatty compounds. The idea is undoubtedly an advance on the simple summation law advanced by Kopp; but it is doubtful whether the value for the successive increase of CH_2 can be accurately determined, since measurements of molecular volume by different observers frequently differ by 0·5 unit. It is remarkable that the expansion of the CH_2 value disappears when the comparison is made under other conditions, such as at equal temperatures,[1] or in some cases at the melting-point.[2]

Isomerides.[3]—Kopp recognized that isomerides of widely

[1] Horstmann, *Beziehungen zwischen der Raumerfüllung und chemischer Zusammensetzung;* Graham-Otto, *Lehrbuch der Chemie,* vol. i. 3, 1898.

[2] Krafft, *Ber.,* 15, 1711 (1882); 17, 1371 (1884); also see p. 137.

[3] Brown, *Proc. Roy. Soc.,* 26, 247 (1878); Dobriner, *Ann.,* 243, 30 (1888); Feitler, *Zeit. Phys. Chem.,* 4, 66 (1889); Gartenmeister, *Ann.,* 233, 249 (1886); Neubeck, *Zeit. Phys. Chem.,* 1, 649 (1887); Pinette, *Ann.,* 243 (1888); Ramsay, *Trans. Chem. Soc.,* 35, 463 (1879); Schiff, *Ann.,* 220, 71, 278 (1883); *Ber.,* 14, 2761 (1881); Städel, *Ber.,* 15, 2559 (1889);

different chemical nature have different molecular volumes, but he claimed that those of similar structure had the same molecular volume.   Later work has shown that this is not strictly true.   The following collection of data is divided into three parts; the first contains isomerides taken from different classes of compounds, and the others those of similar chemical structure.

TABLE V.

MOLECULAR VOLUMES OF ISOMERIDES AT THE BOILING-POINT.

Substance.	V_m	B.P.	Substance.	V_m	B.P.
Propyl alcohol .	81·3	97°	Aniline	109·1	183°
Methyl ethyl ether	84·0	10·8°	Picoline. . . .	121·5	133·5°
Hexyl alcohol .	146·0	156·6°	Allyl alcohol . .	74·2	96·6°
Dipropyl ether .	150·1	86°	Acetone. . . .	76·8	56·0°
Anisole . . .	125·2	155°	Aldehyde . . .	56·9	21·0°
o. cresol . . .	121·5	190·8°	Ethylene oxide .	52·4	12·5°

ISOMERIC ESTERS.

$C_7H_{14}O_2$.	V_m	B.P.	$C_8H_{16}O_2$.	V_m	B.P.
Methyl caproate.	172·2	149·6°	Methyl heptylate.	196·2	173°
Ethyl valerate .	174·5	144·6°	Ethyl caproate .	197·7	167°
Propyl butyrate.	174	143°	Propyl valerianate	197·8	167°
Butyl propionate	173·2	146°	Butyl butyrate .	197·8	165·7°
Amyl acetate. .	173·8	148°	Hexyl acetate . .	197·7	169°
Hexyl formate .	173·3	153·2°	Heptyl formate .	196·7	176°

ISOMERIC ETHERS.

Substance.	V_m	B.P.	Substance.	V_m	B.P.
Methyl heptyl ether . . .	194·6	149·8°	Methyl propyl ether	105·1	38·9°
Dibutyl ether .	197·3	140·9°	Diethyl ether . .	106·1	35·0°
Phenetole. . .	148·9	172·0°	Propyl phenyl ether	172·0	190·0°
o. Cresol methyl ether . . .	147·7	175·0°	*p.* Cresol ethyl ether	172·1	190·0°

Thorpe, *Trans. Chem. Soc.*, **37**, 141, 327 (1880);   Zander, *Ann.*, **224**, 74 (1884);   Schröder, *Ber.*, **13**, 1560 (1880).

Several regularities have been detected in the latter class of isomeride. It seems that the difference in volume is connected with the boiling-points of the substances. Dobriner noticed that the alkyl ethers of symmetrical structure boil lower, and have larger molecular volumes than the less symmetrical compounds ; and Gartenmeister observed similar relations with the esters. Whether branching of the carbon chain has a definite influence on volume is not yet clear, but the work of Zander on propyl derivatives shows that the *iso* structure has the smaller density. It may be noted that Brown has found the difference between normal and isopropyl iodide to be very nearly the same at the boiling-point under all pressures. Since the normal propyl compounds have the higher boiling-points, the relation between volatility and volume already noted with the ethers and esters holds with these substances. The rule also applies to certain isomeric halogen derivatives which have been studied by Städel and by Thorpe—

Formula.	B.P.	V_m at B.P.	Formula.	B.P.	V_m at B.P.
CH_3-$CHCl_2$ . .	58°	88·2	CH_3CCl_3 . . .	74°	108·0
CH_2Cl-CH_2Cl .	84°	85·3	$CH_2ClCHCl_2$.	114°	102·7

but it is not universal.

Stereoisomerides.—Walden[1] and Liebisch[2] have compared the densities of optically active substances with the racemic isomerides. In the majority of cases examined, the racemic compound had the greater density, but the difference between them is not great, and the few exceptions may be due to experimental error. The data concerning geometrical iso- merides are very few, but the measurements of Traube[3] with dilute aqueous solutions show that the "trans" modification has usually the greater molecular volume. For example—

[1] *Ber.*, 29, 1699 (1896).
[2] *Ann.*, 286, 140 (1895).
[3] *Ann.*, 240, 43 (1886).

Substance.	V_m	Substance.	V_m	Substance.	V_m
Sodium fumarate	59·4	Sodium mesaconate	70·6	Sodium isocrotonate	64·4
Sodium maleate	54·3	Sodium citraconate	66·5	Sodium crotonate .	62·4

Unsaturation.[1]—The experiments of Buff (1865) showed that the volume of an element varies according to the degree of saturation. This experimenter found that unsaturated carbon compounds generally have greater volumes than would be expected from the summation law of Kopp, and hence formed the conclusion that unsaturated carbon occupies a larger volume than the saturated element. From the study of other elements Buff framed the general rule that the atomic volume diminishes as saturation proceeds. Schiff, some years later, confirmed Buff's conclusion so far as carbon was concerned, and further endeavoured to find a quantitative measure of the volume decrease caused by unsaturation. He assigned a value to ethylenic carbon four units in excess of that of the saturated element. Another attempt to give a numerical expression to the unsaturation of carbon was made by Lossen, only, regarding the question from a different aspect, he associated the increase in volume with removal of hydrogen. For every hydrogen atom removed from the saturated compound, he adds 1·5 units, or for the formation of an ethylenic linking 3 units. The unsaturated substances at the disposal of these chemists were very few, and in some instances the comparisons were incorrectly made. Schiff, for example, seems to have regarded benzene as a saturated substance, but we now know that in chemical behaviour this compound lies between a saturated and a normal unsaturated substance; and since many of its physical properties are anomalous, it cannot be employed to detect the normal effect of unsaturation. At present we must be content with examining some instances

[1] Buff, *Ann. Suppl.*, **4**, 129 (1865); Schiff, *Ann.*, **220**, 301 (1883); Lossen, *Ann.*, **254**, 42 (1889); **214**, 81 (1883); Kraffts, *Ber.*, **17**, 1371 (1884); Zander, *Ann.*, **214**, 138 (1882); Horstmann, Graham Otto, *Lehrbuch der Chemie*, vol. i. **3**, p. 422 (1880).

collected from general literature; but, unfortunately, only a few data referring to the volumes at the boiling-point are available.

TABLE VI.

Saturated compound.	V_m at [1] boiling-point.	Δ	V_m at [1] boiling-point.	Unsaturated compound.
Di-isobutyl . . .	184·5	7·3	177·2	Caprylene
Sec. Pentane . .	117·1	7·2	109·9	Sec. Amylene
Hexane	139·8	2 × 7·2	126·5	Diallyl
Propyl alcohol . .	81·3	7·2	74·1	Allyl alcohol
Propyl ether. . .	150·9	2 × 7·2	135·5	Allyl ether
Propyl acetate . .	128·5	7·1	121·4	Allyl acetate
Propyl chloride. .	91·4	7·2	84·2	Allyl chloride
Propyl bromide. .	97·4	6·9	90·5	Allyl bromide
Propyl iodide . .	106·9	5·7	101·2	Allyl iodide
Methyl propionate.	104·2	5·8	98·4	Methyl acrylate
Ethyl propionate .	127·8	6·1	121·7	Ethyl acrylate

OTHER COMPARISONS AT EQUAL TEMPERATURES.

Substance.	Formula.	T	V_m^T	Δ
Hexane	C_6H_{14}	16°	130·4	7·8
Hexylene	C_6H_{12}	16°	122·6	3·2
Diallyl	C_6H_{10}	16°	119·4	1·7
Hexatriene	C_6H_8	15°	117·7	
Cyclohexane	C_6H_{12}	20°	107·8	6·6
Cyclohexene	C_6H_{10}	20°	101·2	6·9
Cyclohexadiene (1·4) . .	C_6H_8	20°	94·3	5·7
Benzene	C_6H_6	18°	88·6	
Methyl cyclohexane . .	C_7H_{14}	17°	127·0	7·6
Δ² methyl cyclohexene .	C_7H_{12}	15°	119·4	
1·3 dimethyl cyclohexane	C_8H_{16}	18°	144·8	8·8
Δ⁴ 1·3 dimethyl cyclohexene	C_8H_{14}	18°	136·0	
n. Caproic acid	$C_6H_{12}O_2$	20°	125·6	7·2
γ. δ. Hexenic acid . . .	$C_6H_{10}O_2$	21°	118·4	
n. Valerianic acid . . .	$C_5H_8O_2$	20°	108·3	6·7
γ. δ. Pentenic acid . . .	$C_5H_6O_2$	18°	101·6	

[1] See Schiff, *Ann.*, **220**, 71 (1883) ; Zander, *Ann.*, **114**, 138 (1860).

HYDROCARBONS AT THE MELTING-POINT.[1]

Substance	V_m at M.P.	Δ	Substance.	V_m at M.P.	Δ
Dodecane . . .	219·9	8·7	Hexadecane . .	291·4	8·5
Dodecylene . . .	211·2	6·2	Hexadecylene. .	282·9	6·8
Dodecylidene . .	205		Hexadecylidene .	276·1	
Tetradecane . .	255·4	8·5	Octadecane . .	326·9	8·3
Tetradecylene . .	246·9	6·4	Octadecylene . .	318·6	6·8
Tetradecylidene .	240·5		Octadecylidene .	311·8	

From the numerous instances quoted, there can be no doubt that unsaturation causes a contraction in molecular volume, but whether this is approximately constant for different classes of compounds, or even for homologues, is very doubtful. In the above table several different methods of comparison are employed : at the boiling-point and melting-point, and at arbitrary temperatures ; but it is only at the melting-point that the effect of unsaturation is approximately constant. Here we find that on passing from the saturated substance to the ethylene derivative there is a regular decrease of about 8·5 units in volume ; moreover, the second stage of unsaturation—the change of ethylenic to acetylenic structure—is accompanied by a decrease of molecular volume, but this is less than in the first stage, being now about 6·5 units. The effect of accumulating ethylenic linkages is illustrated with the hexane series ; it is evident that each successive double linkage has less effect than the preceding one ; this does not hold with the derivatives of cyclohexane, but it should be remembered that the properties of benzene are abnormal.

Ring-formation.—The contraction which accompanies the conversion of a paraffin to a cycloid hydrocarbon is considerably larger than that caused by unsaturation. The accompanying list affords illustration of this ; and the column under Δ shows the effect of ring-formation.

In the homologous cycloparaffins, the effect seems to increase with molecular weight ; cyclononane is exceptional,

[1] Kraffts, *Ber.*, 17, 1371 (1884).

but there is reason to doubt the purity of the sample employed.[1] In all the cases examined, the decrement for ring-formation is larger than would be caused by the mere removal of two hydrogen atoms (11·0 according to Kopp), hence it follows that the contraction observed is at least partially due to the cyclic arrangement. Similar reasoning applied to the effect of unsaturation shows that unsaturated carbon occupies a larger volume than the saturated element; thus, the effects of ring-formation and unsaturation would be of opposite nature, whereas with every other physical property they are similar. The anomaly is removed by assuming for hydrogen the value (2·97) calculated by Le Bas[2] from the paraffins; unsaturated carbon is then seen to occupy a smaller volume than when saturated.

TABLE VII.

Paraffin.	Formula.	V_m°.	Δ	V_m°.[2]	Formula.	Substance.
Butane .	C_4H_{10} .	96·5	−17·5	79·0	C_4H_8 .	Cyclobutane
Pentane .	C_5H_{12} .	112·4	−21·3	91·1	C_5H_{10} .	Cyclopentane
Hexane .	C_6H_{14} .	127·2	−22·0	105·2	C_6H_{12} .	Cyclohexane
Heptane .	C_7H_{16} .	142·5	−24·5	118·0	C_7H_{14} .	Cycloheptane
Octane .	C_8H_{18} .	158·3	−27·4	130·9	C_8H_{16} .	Cyclooctane
Nonane .	C_9H_{20} .	174·3	−14·8	159·5	C_9H_{18} .	Cyclononane
Decane .	$C_{10}H_{22}$.	190·2	3×16·7	140	$C_{10}H_{16}$.	Tricyclodecane
Menthone	$C_{10}H_{18}O$	172(15°)	−13	159(15°)	$C_{10}H_{16}O$	Carone

§ 5. *CRITICAL CONSTANTS*

The relations between the molecular critical volumes of homologues and of isomerides are similar to those already noticed with molecular volumes at the boiling-point. The following values have been calculated from the most reliable data :—

[1] Willstätter, *Ber.*, **41**, 1480 (1908).
[2] *Trans. Chem. Soc.*, **91**, 112 (1907).
[3] Willstätter and Bruce, *Ber.*, **40**, 3981 (1907).

TABLE VIII.

CRITICAL VOLUMES.

HOMOLOGUES.

Substance.	$V_K \times M.$	Δ	Substance.	$V_K \times M.$	Δ
Methyl formate .	172		Pentane . . .	310	
Methyl acetate .	227	55	Hexane. . . .	367	57
Methyl propionate	282	55	Heptane . . .	427	60
Methyl butyrate .	340	58	Octane	489	62

ISOMERIDES.

	$V_K \times M.$		$V_K \times M.$
Methyl acetate	227 ⎱	Isoamyl formate . . .	411 ⎱
Ethyl formate	229 ⎰	Isobutyl acetate . . .	412 ⎰
Ethyl acetate.	286 ⎫	Ethyl butyrate	420 ⎱
Methyl propionate . . .	282 ⎬	Ethyl isobutyrate . . .	420 ⎰
Propyl formate	284·5 ⎭		

Critical Coefficients.—According to the theories of Clausius, Mosotti, and Exner,[1] the expression—

$$\frac{n^2 - 1}{n^2 + 2} \quad {}^{*}$$

represents the ratio of the volume actually occupied by matter to the apparent volume of the substance. The product of this and the molecular volume

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

will therefore be a measure of the space filled by matter in a gram-molecule of a substance.[2] We may therefore expect to

[1] Exner, *Wien. Ber.*, **91**, 850 (1885).

* n^2 represent the refractive index for waves of infinite length, n being taken as equal to the dielectric constant.

[2] Guye, *Ann. Chim. Phys.*, [6] **21**, 208 (1890).

find a constant relation between the molecular refraction and the three magnitudes: b of van der Waals' equation, the critical volume, and the critical coefficient. This is confirmed by experiment. Traube [1] has shown that b is approximately 3·5 times as large as the molecular refraction, whilst Guye,[2] comparing this with the critical coefficient, finds the constant relation—

$$MR = 1·8 \frac{T_K}{P_K}$$

For example :—

Sulphur dioxide	crit. coeff. ÷ mol. ref.	=	1·8
Hydrochloric acid gas	,,	,,	= 1·9
Acetone	,,	,,	= 1·7
Triethylamine	,,	,,	= 1·8
Thiophene	,,	,,	= 1·9

Now, since the molecular refractivity is approximately equal to the sum of the atomic refractivities modified by certain constants depending on the structure of the molecule, it follows that by dividing the atomic refractivities by 1·8 we shall obtain the atomic critical coefficients. Guye finds the following values for these atomic coefficients.

ATOMIC CRITICAL COEFFICIENTS.[3]

C = 1·35	Cl. = 3·27
H = 0·57	Br. = 4·83
O' = 0·87	I⁼ = 6·88
O'' = 1·27	I.⁼ = 1·03

[1] *Drud. Ann.*, **5**, 552 (1901).

[2] *Ann. Chim. Phys.*, [6] **21**, 222 (1890).

[3] These numbers are based on the atomic refractivities calculated by Landolt (*Ann.*, **213**, 75, 1882) for light of infinite wave length from the formula

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \text{etc.}$$

From these values the critical coefficient of a substance may be roughly calculated, *e.g.*—

Ethyl acetate $C_4H_8O'O''$

$$4C = 5\cdot40$$
$$8H = 4\cdot56$$
$$O' = 0\cdot87$$
$$O'' = 1\cdot27$$

$C_4H_8O'O'' = 12\cdot10$ Experiment gives $12\cdot0-12\cdot4$.

§ 6. *MOLECULAR AND ATOMIC CO-VOLUME*

We have hitherto confined our attention as closely as possible to the volume actually occupied by the molecule; nothing has been said of the space which the molecule inhabits by virtue of its vibrations. In the equation of van der Waals the sphere of vibration of the molecules is represented by the factor $(V-b)$, and this, for gram-molecules of gases under equal conditions of pressure and temperature, has a constant value. Traube[1] has applied this notion to liquids, and he claims to have shown that the vibration sphere, or co-volume, is constant for gram-molecules of different liquids under equal external conditions. The molecular co-volume of a gram-molecule of a substance is usually represented by ϕ; we may write—

$$V_m = \Sigma nVa + \phi$$

where the assumption is made that the sum of the volumes of the atoms (V_a) equals that of the molecule. We may now briefly examine the chain of reasoning constructed by Traube in forming this conclusion.

In associated substances it may be assumed that the complex molecules have the same vibration sphere as the simple ones, and hence, when a monomolecular liquid undergoes

[1] *Ueber den Raum der Atome*, Stuttgart, 1899, p. 29; *Ber.*, **25**, 2524 (1892); **27**, 3173 (1894); **28**, 2722, 3292 (1895); *Zeit. Anorg. Chem.*, **3**, 1 (1892); **8**, 12 (1895); *Ann.*, **290**, 44 (1895); *Wied. Ann.*, **61**, 380 (1897); **62**, 490 (1897).

polymerisation, the value of ϕ and consequently the molecular volume will be diminished. At the outset of his investigations Traube devoted his attention to finding a means of eliminating this disturbing effect of association, and he insists that this may be done by measuring the molecular volume in dilute aqueous solution. If m is the molecular weight of a dissolved substance in grams, l the quantity of solvent which is present for every gram-molecule of solute, d the density of the solvent, and d_s the density of the solution, then the "molecular solution volume" [1] $_sV_m$ is related to these as follows :—

$$_sV_m = \frac{m + l}{d_s} - \frac{l}{d}$$

From the molecular solution volumes of a large number of substances, Traube calculated the atomic volumes of the elements and the volume effects of a few of the chief modifications of structure. These are collected in the annexed table—

TABLE IX.

Atom.	Sol. vol. in c.c. at 15°.	Atom.	Sol. vol. in c.c. at 15°.
Carbon	9·9	Chlorine	13·2
Hydrogen	3·1	Bromine	13·2
Oxygen(OH of COOH)	0·4	Iodine	13·2
Oxygen (OH) . . .	2·3	$C \equiv N$	13·2
Oxygen (CO) . . .	5·5	Nitrogen (N''') . .	1·5
Sulphur (SH) . . .	15·5	Ring-formation . .	−8·1
Sulphur (SO') . . .	10–11	Unsaturation . . .	No effect
Nitrogen (NO₂) . .	8·5–10·7		

If we now attempt to reconstruct the molecular solution volume of a substance from these values, we find that the sum of the atomic constants is less than the molecular solution volume of experiment by a constant amount. For example, take methyl alcohol :

[1] The volume occupied by a gram-molecule of the substance in solution.

$$CH_3OH : {}_sV_m \text{ (calc.)} = 9\cdot9 + 4 \times 3\cdot1 + 2\cdot3 = 24\cdot6$$
$${}_sV_m \text{ (obs.) at } 15° = \underline{37\cdot0}$$
$$\Delta = \overline{12\cdot4} \text{ c.c.}$$

The values of Δ for a few other substances are given below, and the average is about 12·4 cubic centimetres—

	Δ		Δ
Isoamyl alcohol . .	12·2	Glycerine	12·3
Isopropyl alcohol . .	11·9	Erythrite	12·6
Allyl alcohol	12·7	Propyl alcohol . . .	12·4

This increment of molecular volume over the atomic volumes may be called the molecular solution co-volume.

The molecular solution volume must not be confused with the molecular volume of a homogeneous liquid. Traube finds that a substance contracts on passing into solution, and the molecular contraction is approximately constant. When the molecular solution volumes of a non-ionised acid and the completely ionised sodium salt are compared at 15°, it is found that the volume of the latter is uniformly the smaller by about 15 c.c. Subtracting from this value the diminution in volume caused by replacing hydrogen by sodium (1·5 c.c.), we obtain 13·5 c.c. as the contraction due to the dissociation of a binary electrolyte. Traube regards this diminution in volume as due to osmotic pressure, which, according to Barmwater,[1] is a direct measure of the attraction between the molecules of solvent and solute. Now, since there is a contraction of 13·5 c.c. when two ions are formed from one undissociated molecule, we must expect the same contraction to take place where a gram-molecule of a non-electrolyte is dissolved, for the same change in osmotic pressure is produced. To obtain the molecular co-volume of a homogeneous liquid we must therefore add this 13·5 c.c. to the molecular solution co-volume. Hence the molecular co-volume at 15° is approximately 12·4 + 13·5 = 25·9 c.c.

This conclusion is confirmed by comparing the sum of the atomic volumes with the molecular volume of a liquid; the difference is approximately 25–26 c.c. ; for example—

[1] *Zeit. Phys. Chem.*, **28**, 115 (1899).

TABLE X.

Substance.	$\phi = V_m - \Sigma_n V_a$	Substance.	$\phi = V_m - \Sigma_n V_a$
n. Heptane . . .	26·0	Diethyl succinate .	25·8
Octyl chloride . .	24·0	Lauronitrile . .	25·6
Ethyl ether . . .	26·7	Propyl benzoate .	25·0
Octyl propionate .	26·1	Dodecane . . .	25·3
Butyric anhydride .	26·0	Isobutyl mustard oil	25·0

We see, then, that the molecular co-volume is approximately the same for widely different classes of compounds. It may be noted that Traube has dealt with solids in a similar manner, and has found that here the co-volume is almost the same as with liquids.

For convenience the numerical relations between the molecular solution co-volume and ϕ of homogeneous liquids are summarised below—

Molecular solution co-volume = 12·4 c.c. at 15° C.

Molecular solution contraction, or contraction caused by dissociation of $\Big\}$ = 13·5 c.c. at 15° C. binary electrolyte

Molecular co-volume = 25·9 c.c. at 15° C.

Atomic Co-volume.—Quite recently[1] Traube has extended the hypothesis of space incompletely filled by matter to the atomic volumes. He distinguishes between the external and internal volume of an atom. The internal or nuclear atomic volume is the space actually filled by the mass of the atom, whilst the external volume is the nuclear volume increased by the volume of a shell of combined ether. It may be noted that the external atomic volume is represented in the equation of van der Waals by *b*, which is 3·5–4 times as large as the nuclear volume.[2] The difference between the external and nuclear volumes—or the volume of the combined ether—is called the *atomic co-volume*, and according to Traube, this is

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[1] *Ber.*, **40**, 130, 723, 724 (1907); *Drud. Ann.*, **22**, 519 (1907).

[2] Traube, *Drud. Ann.*, **5**, 552 (1901).

the space occupied by the active electrons which endow the atom with valency.   Unlike the molecular co-volume, the atomic co-volume varies in size, and Traube has shown that it is proportional to the nuclear volume and to the valency of the atom.   Before considering the means by which this interesting result has been attained, it is expedient to review the conclusions from other lines of research which have converged upon the same question.

§ 7. *THE STERE*

Kopp and Schröder began their researches on volume relations almost simultaneously, but their views were by no means in harmony.   Both, indeed, concurred in the assumption that the molecular volume of a compound is equal to the sum of the volumes of the component atoms; but whilst Kopp assumed that a given element has a constant volume under similar structural conditions throughout all compounds, Schröder thought that atomic volume is variable.   Thus, with the oxides of copper, the molecular volumes are—

$$Cu_2O = 24\cdot86$$
$$CuO = 12\cdot35 \text{ or } Cu_2O_2 = 24\cdot70$$

It is clear that equal volumes of these oxides contain equal quantities of copper, and if it be assumed that the volume of the copper in each is the same, it follows that the volumes occupied by a gram-atom of oxygen are in the simple ratio of 1 to 2.

The outstanding feature of Schröder's[1] views is that the atomic volume, although variable, is always a simple multiple of a certain volume unit called the stere.   The stere is not the same for all elements, but it varies within quite narrow limits.   Further, when two elements are combined, one of them assumes the volume unit of the other; the stere of one of the elements seems to dominate the volume of the compound.   Thus, the molecular volume of a substance may be

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[1] See *Pogg. Ann.*, **56**, 553 (1840); *Wied. Ann.*, **4**, 435 (1898); **11**, 997 (1880); **14**, 656 (1881); *Ber.*, **10**, 848, 1871 (1877).

represented as a simple multiple of the stere of one element contained in it. The compounds of silver may be taken in illustration. The silver stere is 5·14, and the atomic volume is twice this, 10·28; hence metallic silver occupies two steres. With the compounds we have—

Silver oxide . . V_m (obs.) $= 30·8$; stere value $= 6 \times 5·14 = 30·8$
Silver chloride . V_m (obs.) $= 25·8$;   ,, $= 5 \times 5·14 = 25·7$
Silver bromide . V_m (obs.) $= 29·7$;   ,, $= 6 \times 5·14 = 30·8$
Silver iodide . V_m (obs.) $= 41·8$;   ,, $= 7 \times 5·14 = 41·1$

whence it is evident that the volume of oxygen is 2, chlorine 3, bromine 4, and iodine 6 silver steres.

Also with liquid organic compounds, Schröder[1] found that the molecular volume may be regarded as a multiple of a volume unit; but this stere varies slightly—from 6·7 to 7·4— in different classes of compounds, and it does not seem to be determined by any particular element. The molecular volumes of the homologous fatty acids and alcohols show that the value of CH_2 is approximately 21. Now, since formic acid (CH_2O_2) has the molecular volume 41·8 or $2 \times 20·9$, and methyl alcohol (CH_4O) that of 42·7 or $2 \times 21·4$, it follows that in the former substance the volume of CH_2 equals that of O_2, and in methyl alcohol CH_2 occupies the same space as H_2O. The comparison of acetic acid $(C_2H_4O''O' = 63·5)$ with acetaldehyde $(C_2H_4O'' = 56·9)$ shows that the value of hydroxylic oxygen is 6·6, or approximately 7 units; and since the volume of H_2O is 21·4, it is clear that hydroxylic oxygen and hydrogen occupy the same space. This volume (approximately 7) is chosen as the stere. Since $CH_2 = 21$, it is evident that carbon also occupies one stere; and from the relation $CH_2 = O''O' = 21$, we further have ketonic oxygen equal to two steres. Summing up these relations, we may write—

$$C = H = O' = \tfrac{1}{2}O'' = 1 \text{ stere}$$

We thus have the general rule that the number of steres in a saturated compound of oxygen, hydrogen, and carbon is

[1] *Wied. Ann.*, **11**, 997 (1880); **14**, 656 (1881); *Ber.*, **18** 1560 (1886).

equal to the number of component atoms increased by as many steres as there are carbonyl groups. Thus—

Ethyl Alcohol :
$C_2H_6O' = 9$ steres V_m (calc.) $= 63$ approx. V_m (obs.) $= 62\cdot2$

Acetic Acid :
$C_2H_4O''O = 9$ steres V_m (calc.) $= 63$ approx. V_m (obs.) $= 63\cdot5$

With unsaturated compounds an extra stere must be added for every ethylenic linkage. As previously mentioned, the size of the stere is not constant, but we may note that it appears to be subject to definite constitutive influences. In homologous series it increases with rising molecular weight ; thus, according to Ostwald,[1] for the fatty acids we have the sequence :

$$\text{Fatty acids—} \quad \overset{C_1}{6\cdot97,} \ \overset{C_2}{7\cdot06,} \ \overset{C_3}{7\cdot11,} \ \overset{C_4}{7\cdot19,} \ \overset{C_5}{7\cdot24,} \ \overset{C_6}{7\cdot24}$$

Secondary and tertiary derivatives have smaller steres than the normal. Of the chief classes of compounds, the hydrocarbons have the smallest steres ($6\cdot8$–$7\cdot2$), then follow the acids ($6\cdot9$–$7\cdot24$), and, finally, the esters ($7\cdot04$–$7\cdot97$). It is worth observing that exactly similar relations were found[2] with solid organic substances ; but the stere was somewhat smaller, being about $5\cdot0$ units.

It is evident that the relations brought to light by Schröder are of a fundamental character ; and although it is impossible to find any definite physical interpretation for them, they seem to contain the germs of a comprehensive law governing volume and chemical composition. In the present connection the only relevant deduction that can be made is that in compounds the volumes of equivalents of different elements are approximately equal, or stand in some simple ratio to one another. We thus have some indication of an intimate connection between volume and valency.

[1] *Lehrbuch der Allgem. Chem.*, vol. i. 387 (1891).
[2] Schröder, *Ber.*, **10**, 1848, 1871 (1877).

§ 8. *VOLUME AND VALENCY*

It is only recently that the efforts of Barlow and Pope,[1] of Le Bas[2] and of Traube[3] have brought to light the simple relationship between these properties of the atom. The evidence adduced by Barlow and Pope is drawn from the study of the structure of crystals. These investigators adopt the fundamental conception that in a crystalline compound an atom occupies a definite space or sphere of influence; and it is clear that the manner in which these atomic domains are arranged in space will determine the shape of the whole molecule. Further, it is assumed that the atomic spheres are held together in stable equilibrium by the balanced action of attractive and repellant forces between the atoms; they are closely packed together, and are therefore not completely spherical in shape; their condition may be readily pictured by imagining a number of incompressible, but deformable, spheres to be squeezed together, so that the interstices are filled. A crystalline substance possesses a homogeneous structure which must be obtained by the symmetrical arrangement of the atomic spheres of influence.

Now, it is evident that any symmetrical and homogeneous close-packed collection of atomic domains can be divided up into units which will represent in composition and configuration the chemical molecule, and, moreover, the dimensions of each of these units will be in accordance with the crystal form of the substance. From the simple assumption that the volume of the atomic domain is proportional to the valency of the atom, Barlow and Pope proceed to build up structures representing various chemical molecules; then, by assembling these in a homogeneous and symmetrical close-packed arrangement, they deduce the dimensions of the crystalline form of each substance. In all the instances studied—and they are numerous, and drawn from very different classes of compounds—the

[1] *Trans. Chem. Soc.*, **89**, 1675 (1906); **91**, 1150 (1907); *British Association, Section B*, Leicester (1907).

[2] *Trans. Chem. Soc.*, **91**, 112 (1907).

[3] *Ber.*, **40**, 130, 723, 734 (1907); *Drud. Ann.*, **22**, 519 (1907).

theoretical crystal dimensions accord well with those found by experiment. We must here confine our attention to the simplest illustrations. If we construct a homogeneous assemblage of equal spheres packed together as closely as possible, it is found that the dimensions of the arrangement must show either holohedral cubic or hexagonal symmetry. It is also found that the axial ratio of the hexagonal assemblage must be either

$$a : c = 1 : 0.8165, \text{ or } 1 : 1.4142$$

Now, there are two kinds of substance in which the atomic domains will be of equal size : the elements and binary compounds of two elements of the same valency. If the previously described conception of crystalline structure is correct, and if the volume of the atomic domain is proportional to the valency of the atom, it follows that the crystalline forms of these substances must be either cubic or hexagonal. The demands of theory are fully satisfied by the data of experiment. Forty crystalline forms of the elements have been measured, and of these 20 are cubic and 14 hexagonal, the axial ratios of the latter approximating to those required by theory. The six remaining crystal-forms are either pseudo-cubic or pseudo-hexagonal; for example, monoclinic sulphur shows—

$$a : b : c = 0.9908 : 1 : 0.998 \text{ and } \beta = 95° 46'$$

But the exceptional behaviour of these six forms may be readily explained by the assumption that the atomic spheres form groups analogous to molecular aggregates, so that in the close-packed homogeneous assemblage some of the spheres will have a slightly different situation ; the result would be that the symmetry of the arrangement in which all the spheres are similarly placed would be slightly disturbed.

Turning to the binary compounds of elements, we find that 88 per cent. of the known forms [1] are either cubic or hexagonal, but practically all those composed of elements of equal valency crystallise in either of these two systems. Inspection of the

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[1] Retgers, *Zeit. Phys. Chem.*, **14**, 1 (1894).

following list of the hexagonal compounds will show that the axes of these possess the required ratios.

GlO	$a:c = 1·6305$
ZnO	$a:c = 1·6077$
ZnS	$a:c = 0·8175$
CdS	$a:c = 0·8109$
AgI	$a:c = 0·8196$

It is interesting to notice that many of these binary compounds do not exhibit the holohedral symmetry required by a homogeneous and symmetrical close-packed assemblage of spheres of equal size, but they instead exhibit hemihedrism, or tetartohedrism. Barlow and Pope show that this state of affairs is to be expected if the symmetrical arrangement is made up of two kinds of spheres which are of slightly different size; evidently these correspond to the two kinds of elements present. With the elements there is no reason to suppose that the size of the spheres should vary, and with these it is found that holohedrism is general.

Barlow and Pope offer further and independent proof of the relation between valency and volume by showing that the geometrical laws which govern the replacement of spheres in a close-packed assemblage by others of different size, run parallel to the chemical laws which determine the relations between the valencies of the elements which may replace one another in a compound. The strict analogy between the two series of laws adds further strength to the conclusion that the valency of an atom is proportional to the space occupied by that atom in a crystalline structure.

Strict accuracy is not claimed for this law, and in this connection the previously mentioned occurrence of hemihedrism and tetartohedrism in binary compounds of *equi*-valent elements may be recalled. This can only be explained by assuming the domains of the two elements to be slightly different in size. Barlow and Pope have thus been able to compare the sizes of the domains of equivalent atoms. The halogens fall into the order—

$$F < Cl < Br < I$$

and the alkali metals as follows—

$$K < Rb < Cs$$

Barlow and Pope consider that this variation in the size of the atomic spheres of influence affords an explanation of many chemical facts. For example : the maximum number of chlorine atoms with which iodine unites is three in the compound ICl_3; but with fluorine, whose sphere of influence is smaller than that of chlorine, the compound IF_5 is formed.

Further evidence of the correlation between valency and volume has been adduced by Traube from the refractive power of substances. According to the calculations of van der Waals and others,[1] the factor b in the equation—

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

is about four times as great as the sum of the internal volumes of the atoms in a substance. Now, Traube has shown[2] from experimental data that b is between 3·5 and 4 times as large as the molecular refractive power (n^2 formula) of a compound, and thus support is given to the Clausius-Mosotti-Exner theory,[3] which states that the molecular refraction, measured by the Lorenz-Lorentz formula,[4] is approximately proportional to the volume occupied by the atoms. Traube therefore employs the molecular refraction as a measure of the nuclear volumes of the atoms contained in a substance, and he finds that the molecular refractive power of a saturated compound is proportional to the total number of valencies of the component atoms. Some examples are collected in the list on p. 135.

Under n the total number of valencies in the compound is given, and in the right-hand column the quotient : molecular

[1] Van der Waals, *Die Kontinuität des gasförmigen und flüssigen Zustandes*, Leipzig, 1881 ; O. E. Meyer, *Die Kinetische Theorie der Gase*, p. 298, Breslau, 1877 ; also *Stoichiometry*, p. 200, by Dr. Young in this series, 1908.

[2] *Drud. Ann.*, **5**, 552 (1901).

[3] See Exner, *Wien. Ber.*, **91**, 85 (1885); and *Monatshefte für Chemie*, **6**, 249 (1885).

[4] See p. 242.

refraction $\div n$, is shown. The latter is approximately constant, and the average value calculated from a large number of compounds is 0·787; this is called the refraction stere. The valencies assigned to the different elements in these compounds are as follows: H and F = 1, O = 2, N, P, and B = 3, C and Si = 4, Cl = 7; and these, with the exception of that of chlorine, are the usually accepted fundamental valencies.

TABLE XI.

Substance.	Formula.	M_a.	n	Stere.
n. Pentane	C_5H_{12} . .	25·32	32	0·791
n. Hexane	C_6H_{14} . .	27·70	38	0·782
Ethyl alcohol . . .	C_2H_6O . .	12·71	16	0·794
Trimethyl carbinol . .	$C_4H_{10}O$ . .	22·09	28	0·789
Ethyl ether	$C_4H_{10}O$ . .	22·31	28	0·797
Isovalerianic acid . .	$C_5H_{10}O_2$.	26·72	34	0·786
Ethyl acetate	$C_4H_8O_2$ . .	22·14	28	0·791
Glycerine	$C_3H_8O_3$ . .	20·41	26	0·785
Ethyl carbonate . . .	$C_5H_{10}O_3$.	28·22	36	0·784
Isoamylamine	$C_5H_{13}N$ . .	28·53	36	0·793
Tri-isobutylamine . .	$C_{12}H_{27}N$ . .	61·07	78	0·783
Acetonitrile	C_2H_3N . .	11·05	14	0·790
Piperidine	$C_5H_{11}N$ . .	26·52	34	0·780
Amyl nitrite	$C_5H_{11}NO_2$.	31·44	40	0·786
Ethyl chloroacetate .	$C_4H_7ClO_2$.	26·79	34	0·788
Propyl chloride . . .	C_3H_7Cl . .	20·75	26	0·798
Methyl fluoracetate .	$C_3H_5O_2F$.	17·83	22	0·810
Triethyl phosphate . .	$PO(OC_2H_5)_3$	41·79	52	0·803
Triisobutyl borate . .	$B(OC_4H_9)_3$.	66·01	84	0·785
Tetraethyl silicate . .	$Si(OC_2H_5)_4$.	51·71	64	0·806

From these considerations, it follows that the nuclear volumes are proportional to the valencies of the atoms, and thus we have further support for the law deduced from the crystalline structure of compounds.

From this relation Traube has made further deductions which, although somewhat speculative, are of great interest, since they seem to throw light on the structure of the atom. According to the electronic theory, atoms are composed of electrons or groups of electrons, some of which are arranged in a system of stable equilibrium and are inactive, whilst

others, remaining free to combine with other groups of electrons, endow the atoms with valency. Traube terms an active group of electrons a "valon," and he assumes that the nuclear volume is made up of the inactive system of electrons, the valons occupying the atomic co-volume. Translating into these terms the law that the nuclear volume of an atom is proportional to the valency, we see that the nuclear atomic volume is proportional to the number of valons which surround it, and, further, that the space occupied by a valon in the atom is approximately constant. If, as Traube assumes, the b of van der Waals' equation is equal to the sum of the external volumes of the atoms, we can obtain from the expression $b - M$ a measure of the sum of the atomic co-volumes [1]; and, moreover, the quotient of $b - M_a \div n$, where n is the total number of valencies, will represent the average volume of a valon in the substance. The annexed table shows the results of this calculation with several substances; it is evident that this valon-stere roughly approximates to the value $1\cdot 70$. It may be noted that the value of b is taken as equal to the molecular volume at the absolute zero,[2] since at this temperature the v in Van der Waals' equation becomes equal to b.

TABLE XII.

Substance.	Formula.	b_0.	M_a.	$b_0 - M_a$	n	$\dfrac{M_a}{n}$	$\dfrac{b_0 - M_a}{n}$
Pentane	C_5H_{12}	80·2	25·32	54·88	32	0·791	1·72
Hexane	C_6H_{14}	94·8	29·70	65·10	38	0·782	1·71
Octane	C_8H_{18}	123·5	38·95	84·55	50	0·779	1·67
Ethyl ether	$C_4H_{10}O$	72·2	22·31	49·89	28	0·797	1·78
Propyl acetate . . .	$C_5H_{10}O_2$	86·2	26·83	59·37	34	0·789	1·75
Methyl isovalerate .	$C_6H_{12}O_2$	99·4	31·46	67·94	40	0·789	1·69
Propylamine . . .	C_3H_9N	59·6	19·31	40·29	24	0·804	1·87
Diethylamine . . .	$C_4H_{11}N$	74·0	24·07	49·93	30	0·802	1·66
Triethylamine . . .	$C_6H_{15}N$	102·8	33·50	69·30	42	0·799	1·65

Comparison of the columns under $\dfrac{M_a}{n}$ and $\dfrac{b_0 - M_a}{n}$

[1] M_a is the molecular refractivity measured for the a hydrogen line.

[2] From the calculations of Berthelot, *Compt. Rend.*, **130**, 713 (1900); and Guldberg, *Zeit. Phys. Chem.*, **32**, 116 (1900).

shows that the influence which decreases the valon-stere increases the refraction-stere. Traube considers that this is due to the opposed actions of the affinity pressure, which unites the atoms and contracts the valon-stere, and an intra-atomic pressure which tends to expand the nuclear volume.

We may conclude this examination of the evidence showing the proportionality between valency and volume by noting that recently advanced by Le Bas [1] from the molecular volumes of the paraffins at their melting-points. Le Bas compares the molecular volumes of these substances at their melting-points, since the temperatures are then approximately equal fractions of the boiling temperatures, and consequently also of the critical temperatures. It is found that the quotient obtained by dividing the molecular volume by the total number of valencies of the carbon and hydrogen atoms present is constant; thus:

TABLE XIII.

Substance.	Formula.	n	V_m.	$V_m CH_2$.	$V_m \div n$.
Undecane	$C_{11}H_{24}$	68	201·4		2·962
Dodecane	$C_{12}H_{26}$	74	219·9	18·5	2·971
Tridecane	$C_{13}H_{28}$	80	237·3	17·4	2·966
Tetradecane . . .	$C_{14}H_{30}$	86	253·4	18·1	2·970
Pentadecane . . .	$C_{15}H_{32}$	92	273·2	17·8	2·970
Hexadecane . . .	$C_{16}H_{34}$	96	291·2	18·0	2·971
Heptadecane . . .	$C_{17}H_{36}$	104	309·0	17·8	2·971
Octadecane . . .	$C_{18}H_{38}$	110	326·9	17·9	2·972
Nonadecane . . .	$C_{19}H_{40}$	116	344·7	17·8	2·971
Eicosane	$C_{20}H_{42}$	122	362·5	17·8	2·971
Heneicosane . . .	$C_{21}H_{44}$	128	380·3	17·8	2·971
Docosane	$C_{22}H_{46}$	134	398·3	18·0	2·972
Tricosane	$C_{23}H_{48}$	140	416·2	17·9	2·971
Tetracosane . . .	$C_{24}H_{50}$	146	434·1	17·9	2·973
Heptacosane . . .	$C_{27}H_{56}$	164	487·4	53·3	2·972
Hentriacontane . .	$C_{31}H_{64}$	188	558·4	71·0	2·970
Dotriacontane . . .	$C_{32}H_{66}$	194	576·2	17·8	2·970
Pentatriacontane . .	$C_{35}H_{72}$	212	629·5	53·3	2·969
Mean values .	—	—	—	17·83	2·970

Under n and V_m the number of valencies and molecular

[1] *Trans. Chem. Soc.*, **91**, 112 (1907); *Phil. Mag.*, [6] **14**, 324 (1907); **16**, 60 (1908); *Chem. News*, **98**, 85 (1908); **99**, 206 (1909).

volume at the melting-point are respectively placed; and under
$V_m CH_2$ the volume increment per CH_2 is shown.

The average value of $V_m \div n$ is 2·970, and this evidently
represents the volume occupied by one unit of valency in these
substances. The atomic value of hydrogen may be directly
calculated as follows :

$$2H = 2V_m(C_{12}H_{26}) - V_m \, C_{24}H_{50} = 5·7 \text{ or } H = 2·85 ;$$

the mean value being 2·970. Then subtracting $2H$ (5·94)
from the average value of CH_2 (17·83), we have for carbon
$V_m = 11·89$ or $4 \times 2·972$. It is thus evident that the atomic
volumes of carbon and hydrogen are as four to one, and this
is the ratio between their valencies.

§ 9. *COMPRESSIBILITY OF LIQUIDS AND SOLIDS*

When a substance is submitted to increasing external
pressure the volume diminishes, and, as we shall presently
find, the contraction caused by a given increase in pressure
depends to a certain extent on the chemical nature of the
substance. The relative contraction in volume which takes
place on increasing the external pressure by one pressure unit,
is termed the compressibility of the substance. In the measure-
ment of compressibility different units of pressure have been
employed, but the most recent data have been expressed in
terms of the "megabar," which is equal to a pressure of one
megadyne per square centimetre, or 0·987 atmosphere.

The contraction in volume which takes place when increas-
ing external pressure is applied, depends not only on the mag-
nitude of the applied pressure, but also on the internal pressure
which is due to the mutual attraction between the particles of
the substance. If the particles are already tightly compressed
by their mutual affinity, the contraction in volume caused by
applying a given external pressure will be less than when this
cohesional pressure is small. The relation may be illustrated
by comparing the behaviour of gases and liquids. In gases [1]

[1] The compressibility of gases has been fully treated by Dr. Young in
Stoichiometry (this series), p. 19, 1908.

the cohesional pressure is small, and consequently the compressibility is large; on the other hand, the internal pressure of liquids and solids is great, and the compressibility is correspondingly diminished.

These considerations induced Th. Richards[1] to examine the relations between the compressibility of liquids or solids, and their internal pressure. It has been found that this pressure is conditioned by the inter-molecular cohesion, and by the affinity-pressure between the atoms. The relation between compressibility and inter-molecular cohesion is readily seen on comparing the compressibilities and surface tensions of organic liquids.

TABLE XIV.

Substance.	$\beta 10^6$ (100–500 ats.)	γ	L.	$\beta \cdot \gamma^{\frac{1}{3}}$.
Methyl aniline	41·87	39·46	42·67	2·6
m. cresol	42·58	36·82	45·17	2·4
Ethyl acetate	81·6	23·87	30·94	2·6
Ethyl benzene	64·8	28·9	33·88	2·7
Methyl alcohol	85·7	22·39	35·14	2·5
Ethyl bromide	89·5	23·23	27·61	2·8

In the foregoing table the column under $\beta 10^6$ represents the average compressibilities between 100 and 500 atmospheres pressure, that under γ shows the surface tensions in dynes per square centimetre, and that under L shows the latent heats of vaporisation. The figures in the extreme right-hand column represent the value of the empirical expression $\beta \cdot \gamma^{\frac{1}{3}}$. On surveying the table it will be seen that in substances where the surface tension (inter-molecular cohesion) is low, the compressibility is large, and this diminishes with increasing surface tension. However, the values of these properties are not strictly proportional; but evidently there is a close relation

[1] *Zeit. Phys. Chem.*, **40**, 169, 597 (1902); **42**, 129 (1903); **49**, 1, 15 (1904); **61**, 77, 100, 171, 180, 449 (1908); *Zeit. Elektrochem.*, **13**, 519 (1907); *Journ. Amer. Chem. Soc.*, **26**, 399 (1904).

between them since the empirical value $\beta \cdot \gamma^{\frac{1}{3}}$ is approximately constant for all substances, the average being about 2·5. The deviations from the mean value seem to be due to the different constitutions of the liquids. Also it will be seen that the latent heat of vaporisation, which is a measure of the energy required to overcome the cohesional forces of the molecules, shows a similar relation with the compressibility. The same has been noticed with the boiling temperatures of isomeric liquids.

TABLE XV.

Substance.	B.P.	Density at 0°.	β 10⁰
Ethyl butyrate . . .	120°	0·899	93·0
Methyl valerianate . .	127°	0·901	91·0
Isopropyl alcohol . .	83°	0·788	103·0
Propyl alcohol . . .	97°	0·804	97·0

It seems to be a general rule that the less volatile isomeride has the smaller compressibility.

We shall now turn to the relations between affinity-pressure and compressibility. When two elements unite there is a contraction in volume, and this is evidently caused by the pressure of the affinity uniting the elements. If we calculate the difference between the molecular volume of the substance, and the sum of the atomic volumes of the component elements in the free state, we shall obtain the change of molecular volume caused by this affinity pressure. Now, since the heat of formation of the compound is proportional to the work done by the pressure of affinity between the two elements, it is clear that the expression—

$$\frac{\text{volume-contraction}}{\text{heat of formation}}$$

will give a measure of the average compressibility.

Richards obtained the following data from the halides of the alkali metals.

TABLE XVI.

Salt.	Sum of at. vols.	Mol. vol. of salt.	Contraction, C.	Heat of formation, H.	$\dfrac{C \cdot 100}{H}$
LiCl	37·7	20·9	16·8	383	4·4
NaCl	48·7	27·2	21·5	399	5·4
KCl	70·0	37·8	32·2	427	7·6
LiBr	38·8	25·2	13·0	334	3·9
NaBr	49·2	34·2	15·0	359	4·2
KBr	70·5	44·2	26·3	398	6·6
LiI	38·4	33·1	5·3	257	2·1
NaI	49·4	41·4	8·0	289	2·8
KI	70·7	53·8	16·9	335	5·1

On considering any one of these series, it is seen that the compressibility-effect of the common halide must be the same in each member; hence, if the hypothesis relating affinity pressure to compressibility be correct, we must expect to find that the values of

$$\frac{\text{volume-contraction}}{\text{heat of formation}} = \frac{C}{H}$$

for the different salts fall in the same order of magnitude as the compressibilities of the free alkali metals. Inspection of the figures in the column headed $\dfrac{C}{H}$ will show that this is actually the case.[1] The same relation holds in the series of salts containing different halogens combined with a common alkali metal.

This very brief review of the nature of compressibility is sufficient to make clear the important bearing on the relations between volume and chemical constitution which were considered in the earlier portion of this chapter. It is now clear that the volume occupied by an atom in the free condition cannot be the same as in the combined state, since in the latter case it is submitted to the pressure of affinity. It is further evident that the volume of an atom must alter,

[1] The compressibilities of the elements are quoted on p. 110.

although in a lesser degree, according to the mode of combination, for the affinity-pressure will vary according to the nature of the other atoms with which it is combined. In this way it is possible to explain the constitutive nature of these volume relations, and to account for the partial success attained by Kopp in his endeavour to prove the additive nature of the property.

In conclusion, it should be noticed that Richards has discussed the mechanical structure of an atomic assemblage. He considers that the compressibility relations can only be interpreted by the assumption that the atoms are in actual contact with one another, and that they are compressible. The hypothesis that the space occupied by a substance is incompletely filled by matter must be rejected. It is remarkable that this view is in harmony with the fundamental assumptions made by Pope and Barlow in their study of the volume relations of crystalline structures.

Having followed the developments of the relations between volume and constitution up to the most recent stage, we may now briefly examine the methods of applying these relations to the solution of problems met by the chemist in laboratory practice.

§ 10. *THE APPLICATION OF VOLUME RELATIONS*

Traube has turned his discovery of the molecular co-volume to account in determining the molecular weight of substances.[1] The density of the liquid is determined at $15°$, and then with the aid of the constitution of the substance the value of Σnc is calculated from the volume-effects of the component atoms, making allowance for certain structural modifications such as unsaturation and ring-formation. The following table contains the chief atomic volumes and structural corrections necessary; it may be noted that, with the exception of the halogens, they are only slightly different from those already quoted (p. 125) for aqueous solutions.

[1] *Zeit. anorg. Chem.*, **8**, 338 (1895); *Ber.*, **28**, 2728, 2924 (1895); **29**, 1023 (1896); **30**, 265 (1897).

TABLE XVII.

Carbon	$=$	9·9 c.c.	Fluorine . . . . $=$	5·5 c.c.
Hydrogen. . . .	$=$	3·1 c.c.	Chlorine . . . . $=$	13·2 c.c.
O' (in hydroxyl) . .	$=$	2·3 c.c.	Bromine . . . . $=$	17·7 c.c.
O'' $\left(\text{in CO or } O<^C_C\right)$ $=$		5·5 c.c.	Iodine . . . . $=$	21·4 c.c.
			CN . . . . . $=$	13·2 c.c.
O^e (in OH of COOH) $=$		0·4 c.c.	N''' . . . . . $=$	1·5 c.c.
S' (in SH) . . .	$=$	15·5 c.c.	$=$ . . . . . $=$	$-1·7$ c.c.
S'' (in CS) . . .	$=$	15·5 c.c.	$\equiv$ . . . . . $=$	$-3·4$ c.c.
S° (in SO') . . .	$=$	10–11·5 c.c.		

Formation of six-membered carbon ring $= -8·1$ c.c.

If the substance has the simple molecular weight indicated by the empirical formula, the relation—

$$\frac{M}{d} - \Sigma nc = 25·9$$

will hold; but if $M \div d - \Sigma nc$ has a smaller value, then association must be assumed. For examples we may take butyl sulphide, naphthalene, and formic acid.

Butyl sulphide ($C_8H_{18}S$):

8 carbon atoms . . . . . . $= 79·2$

18 hydrogen atoms . . . . . $= 55·8$

1 sulphur atom . . . . . . $= 15·5$

Σnc . . . . . $= 150·5$ c.c.

$V_m = 174·8$ c.c. at 100°; hence—

$V_m - \Sigma nc = 174·8 - 150·5 = 24·3 = \phi$

$\phi = 25·0$ at 100°

Hence butyl sulphide has the simple molecular weight.

Naphthalene ($C_{10}H_8$) :

10 carbon atoms . . . . . . $= 99·0$

8 hydrogen atoms . . . . . $= 24·8$

$123·8$

Subtract for 2 ring systems ⎱
        „ 5 double linkages ⎰ . . $14·7$

Σnc . . . . . $= 109·1$ c.c.

$V_m = 125·9$ c.c. at 19°; $V_m - \Sigma nc = 125·9 - 109·1$ c.c. $= 16·4 = \phi$.

Hence naphthalene has the simple molecular weight.

Formic acid (CH_2O_2):

$$\begin{array}{lr}
\text{1 carbon atom} \ldots \ldots & = 9\cdot9 \\
\text{2 hydrogen atoms} \ldots \ldots & = 6\cdot2 \\
\text{2 oxygen atoms} \ldots \ldots & = 5\cdot9 \\
\hline
\Sigma nc \ldots \ldots & = 22\cdot0 \text{ c.c.}
\end{array}$$

$$V_m (15°) = 37\cdot5 \text{ c.c.} ; \ V_m - \Sigma nc = 15\cdot5 = \phi.$$

Hence the molecular weight is greater than that indicated by the simple formula CH_2O_2, and formic acid is associated.

The method may thus be used to detect association in a liquid; moreover, the degree of association may be approximately determined. If the ϕ of experiment has half the theoretical value : $12\cdot9$ instead of $25\cdot9$, then the molecular weight is twice that assumed in the calculation. Moreover, if the value of $V_m - \Sigma nc$ lies between $12\cdot9$ and $25\cdot9$, the association factor, x, may be calculated from the expression—

$$x = 1 + \frac{25\cdot9 - \phi'}{12\cdot95}$$

where ϕ' is the co-volume calculated from the experimental data with the assumption that the substance has the simple molecular weight.

Traube has submitted many liquids to this test for association; and, qualitatively, the results agree well with the data furnished by the surface energy method of Ramsay and Shields. The left-hand part of the table on p. 145 contains unassociated substances, and it will be seen that, according to both methods, the association factors closely approximate to unity; the right-hand division contains associated compounds.

A similar process may be adopted for ascertaining the molecular weight of a substance in dilute aqueous solution. For dissolved substances we have the relation—

$$_sV_m = \Sigma nc + \phi_s$$

where $_sV_m$ is the molecular solution volume and ϕ_s the molecular solution co-volume; the latter is approximately $12\cdot4$ c.c. at $15°$. It should be remembered that in calculating Σnc the atomic and structural constants for solutions must be used, and

further, if the substance is an electrolyte, allowance must be made for dissociation. The process may be illustrated with sodium cinnamate—

Sodium cinnamate $C_9H_7O_2Na$.

A 2·139 per cent. aqueous solution has $d_{15}° = 1·00685$, whence, assuming the monomolecular weight, $_sV_m = 109·4$ c.c.—

9 carbon atoms	=	89·1	1 ionisation const. =	$-13·5$
7 hydrogen atoms =		21·7	1 six‑membered	
2 oxygen ,,	=	5·9	ring . . . =	$-8·1$
1 sodium ,,	=	1·8		

$$118·5 \text{ c.c.} \qquad\qquad -21·6 \text{ c.c.}$$

$$\Sigma nc = 96·9 \text{ c.c.}$$

$$_sV_m - \Sigma nc = 109·4 - 96·9 = 12·5 \text{ c.c.} = \phi,$$

Hence the assumption of the simple molecular formula is justified.

TABLE XVIII.

Substance.	Association factor.		Substance.	Association factor.	
	R. & S.	T.		R. & S.	T.
Hexane . . .	0·98	0·93	Methyl alcohol .	2·53	1·79
Benzene . . .	1·05	1·18	Propyl alcohol .	1·70	1·66
Toluene . . .	1·01	1·08	Glycol . . .	2·05	1·88
Ethyl formate .	1·08	1·24	Acetic acid . .	2·32	1·56
Propyl acetate .	1·00	1·18	Ethyl alcohol .	1·80	1·67
Ethyl ether . .	1·04	0·94	Water . . .	1·79	3·06
Chlorobenzene .	1·06	1·00	Nitroethane . .	1·28	1·82
Chloroform . .	1·00	1·00	Pyridine . . .	1·00	1·75

Beyond the detection of association, volume relations are of little use in solving questions of constitution; but it may be observed that, if the molecular weight has been determined by other methods, the value of Σnc may be calculated, and from this it might be possible, with simple substances, to interpret the constitution. The prospect of success with such a method

is not very bright, since the distinction between different types of structure—carbonyl and hydroxylic oxygen, for example—is often sufficiently small to be hidden by experimental error or the slight variation in the value of ϕ. Gioletti[1] has applied the process to some tautomeric compounds, and on the whole the results are not very encouraging. Acetoacetic ester has the molecular volume 126·9, whilst the calculated[2] volume for the enolic form is 127·9 and that for the ketonic structure is 132·8. Accordingly it might be supposed that the sample consisted entirely of the enolic tautomeride; but this is contrary to chemical experience and to the evidence from other physical sources. The result seems all the more dubious when it is considered that the addition of piperidine or sodium ethylate does not influence the molecular volume of the ester.

The presence of the cyclic structure should be more easily detected since, according to Traube, it causes a contraction of about eight cubic centimetres in molecular volume. Semmler, in his researches on the ethereal oils, regards[3] an abnormally high density as a general indication of complex cyclic structure.

The molecular solution volumes of several carbohydrates have been measured by Traube,[4] and the values found are lower than those calculated from the sum of the atomic effects—

Arabinose $_sV_m$ (obs.) = 93·2 $_sV_m$ (calc.) = 100
Glucose $_sV_m$ (obs.) = 112·0 $_sV_m$ (calc.) = 116·5
Galactose $_sV_m$ (obs.) = 110·0 $_sV_m$ (calc.) = 116·5

Traube considers that the discrepancy is caused by the conversion of the CO group to the aldehydrol arrangement $\!\!\!>\!C\!\!<^{OH}_{OH}$, but the question has been reopened by Cross and Bevan,[5] who suggest that the similar behaviour of starch and cellulose may be due to ring-formation.
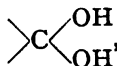
[1] *Gazz. Chim. Ital.*, **34**, 208 (1904).
[2] Traube, *Ber.*, **29**, 1715 (1896).
[3] See *Die aetherische Oele*, vol. i. (1906).
[4] *Ann.*, **240**, 43 (1887).
[5] *Ber.*, **42**, 2198 (1909).

THERMAL PROPERTIES

CHAPTER V

SPECIFIC HEAT AND CHEMICAL COMPOSITION

§ 1. *INTRODUCTION*

WHEN two different bodies at the same temperature are allowed to absorb the same amount of heat, it is usually found that the final temperatures of each are different. We may say that the two bodies require different quantities of heat to raise them through the same range of temperature; in other words, they have different capacities for heat.

The *heat capacity* of an object is the amount of heat which must be supplied to it to raise its temperature through one degree, and it may be expressed by—

$$K = \frac{Q}{t - t'}$$

where Q is the amount of heat absorbed, and t', t the initial and final temperatures. The specific heat of a substance is the heat capacity of unit mass; thus—

$$C = \frac{K}{m} = \frac{Q}{(t - t')m}$$

where m represents the mass of the substance, and it may be defined as the quantity of heat required to raise unit mass through one degree.[1] In expressing quantities of heat it is

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[1] Since specific heat varies with temperature, the above expressions for heat capacity and specific heat really give the mean values of these constants for the interval t' to t. The true specific heat is expressed by $C = \frac{1}{m} \frac{dQ}{dt}$. In practice it is found that the specific heat varies only

usual to employ as a unit the gram calory or the amount of heat required to raise one gram of water through one degree. The *specific heat* then becomes the ratio between the amounts of heat required to raise unit mass of the substance and unit mass of water through one degree.

The *molecular heat*, a quantity much used in comparing the heat capacity of substances, is the heat required to raise one gram-molecule through one degree.

$$C_M = M \cdot C$$

and the *atomic heat* is expressed similarly—

$$C_A = A \cdot C$$

Since water is chosen as the standard, the accurate determination of its specific heat is important. The earliest researches showed that the specific heat of this substance varies with temperature, but at first the results of different observers were not concordant. The more recent measurements by Griffiths,[1] Callendar and Barnes,[2] and Rowland,[3] agree very closely, and since they were obtained by different methods, they are now taken as the basis for accurate determination. A few of the data obtained by these observers are given in the table on p. 149.

On account of this effect of temperature on the specific heat of water, it is necessary, when using that substance as a standard, to choose the specific heat at some definite temperature; but unfortunately the same temperature has not always been adopted. The majority of observers have taken the specific heat of water at some temperature between the ordinary limits 15–18° C., since it is accurately known over this interval, but Griffiths[4] has pointed out that 17–18° C. is the best interval to choose, for the specific heat at this temperature is equal to

slightly over one degree centigrade, so that the mean specific heat for an interval of one degree may be considered equal to the true specific heat at the initial temperature. Thus for water, $C_{18}^{\circ} - _{16}^{\circ} = C_{18}^{\circ}$.

[1] *Phil. Mag.*, [5] **40**, 431 (1895).
[2] *Physical Review*, **10**, 202 (1899).
[3] *Proc. Roy. Soc.*, **61**, 479 (1897).
[4] *Phil. Mag.*, [5] **40**, 431 (1895).

the mean between 0° and 100° C. On the other hand, aniline has been recommended [1] as the standard on account of the ease of obtaining pure aniline, and also of the slight effect of temperature on its specific heat. Reference to the above table of the specific heat of water will show that within ordinary limits the variation is not large; so that for our purpose the choice of the standard temperature of water is not very important.

TABLE I.

SPECIFIC HEAT OF WATER.

Temperature.	Rowland.	Griffiths.	Callendar and Barnes.
10°	1·0019	—	1·0021
12	1·0010	—	1·0011
14	1·0003	1·0003	1·0003
15	1·0000	1·0000	1·0000
16	0·9996	0·9997	0·9997
17	0·9993	0·9994	0·9994
18	0·9990	0·9991	0·9990
19	0·9986	0·9988	0·9988
20	0·9983	0·9985	0·9985
21	0·9981	0·9982	0·9983
24	0·9974	0·9973	0·9975

The question as to the correct temperature at which comparisons between different substances should be made is far more urgent. Here again there is no uniformity in the measurements of different observers; for example, Reis [2] compared the average specific heats between 20° C. and the boiling-point, whilst de Heen [3] measured them between 10° and 50° C.

§ 2. *EFFECT OF TEMPERATURE ON SPECIFIC HEAT OF SOLIDS AND LIQUIDS*

With nearly every substance the specific heat increases with temperature. A few bodies, however, are exceptional in their

[1] Griffiths, *Phil. Mag.*, [5] **39**, 47 (1895).
[2] *Wied. Ann.*, **13**, 447 (1881).
[3] *Essai de Physique Comparée*, Bruxelles, 1883.

behaviour. The specific heat of the monatomic metal mercury decreases with rising temperature, and this has been shown by Heilborn[1] to be in accordance with theory. Sohncke[2] also claims to have proved on theoretical grounds that the specific heat of a substance whose molecules consist of single atoms cannot increase with temperature. In support of this theory Schuz[3] found that the specific heat of cadmium[4] between $-78°$ and $+20°$ is larger than between $+20°$ and $+100°$ C.

Other exceptional cases may be explained by a change in molecular complexity. Thus, the specific heat of water falls with rising temperature until about $30°$ C., when it begins to rise again. Also the specific heat of iron increases up to about $700°$ C., and then falls off suddenly; and this is especially interesting, since at that temperature the metal loses its magnetic properties.

In most cases, however, the specific heat is a linear function of the temperature—

$$C_t = A + Bt$$

Bède[5] first drew attention to this fact with the metals, whilst Schiff[6] claims to have proved it to be a general rule for organic liquids. Table II. contains the constants for a number of substances.

The behaviour of organic liquids, whose specific heats are quoted later, are especially worthy of notice. Schiff[7] has shown that the effect of temperature on specific heat is the same for all substances of the same chemical nature, the only exception being in the fatty acids,[7] in which formic acid has a value for B exactly half that of the other fatty acids.

Dissociation.—The heat which is added to a substance may be distributed in three ways—(1) in performing work against

[1] *Zeit. Phys. Chem.*, **7**, 85 (1891).

[2] *Wied. Ann.*, **66**, 111 (1898).

[3] *Wied. Ann.*, **45**, 184 (1892).

[4] In sodium solution this metal is monomolecular.

[5] *Mémoires Couronnées de l'Acad. de Belg.*, **27**, [2] 1, 1855.

[6] *Ann.*, **234**, 300 (1886); see, however, Kurbatow, *Chem. Centralblatt.*, 1903, I., **571**, 1114.

[7] See p. 166.

external pressure (Q_e); (2) in increasing the kinetic energy of the molecules (Q_h); and (3) in overcoming the mutual attractions of the molecules (Q_m). If in raising one gram of a substance through one degree the quantity of heat Q be added, then—

$$C = Q_e + Q_h + Q_m$$

The quantity of heat, Q_h, employed in raising the temperature of the substance may be called the "true specific heat." If all the heat supplied were used in this way, the experimental value of the specific heat would equal this true specific heat; but of course this is never found in practice. With liquids and solids the value of Q_e is vanishingly small; then

$$C = Q_h + Q_m$$

With associated substances the quantity of heat represented by Q_m in the above expression may be divided into two parts: the heat used in breaking down molecular aggregates, and that employed in overcoming the usual molecular cohesion. If these quantities are represented by Q_{m2} and Q_{m1} respectively, then

$$C = Q_h + Q_{m1} + Q_{m2}$$

TABLE II.

METALS.

C_t.	A.	B.
Mercury	0·033266	− 0·0000092t
Platinum	0·0317	+ 0·0000012t
Iridium	0·0317	+ 0·0000012t
Palladium	0·05820	+ 0·00002t
Silver (0–907°)	0·05758	+ 0·0000088t
Silver (907–1100°)	0·0748	
Nickel (0–230°).	0·10836	+ 0·000044t
Nickel (230–400°)	0·18349	− 0·000056t
Nickel (400–1150°) . . .	0·099	+ 0·0000675t
Gold (100–900° C.) . . .	0·0324	
Iron (0–660°)	0·11012	+ 0·0000209t
Iron (660–720°).	0·57803	− 0·002872t
Iron (720–1000°)	0·218	
Cobalt (0–890°)	0·10584	+ 0·0000457t

Hence, when an associated substance breaks down into simple aggregates on being heated, its specific heat will be greater than if it were unassociated, or if the dissociation did not take place. In other words, we might say that the specific heat at constant association is less than the specific heat during dissociation. We may thus explain the change in specific heat which occurs on passing from one state to another. Many substances have an abnormally high specific heat near the melting-point. In the following table the specific heats of some substances in the liquid and solid states are contrasted, and it will be seen that the liquid has a greater specific heat than the solid.

TABLE III.

Substance.	Solid.		Liquid.	
	Temp.	Spec. heat.	Temp.	Spec. heat.
Ice and water . .	$-78\text{-}0°$	0·474	$15°$	1·00
$CaCl_2 . 6H_2O$ . .	$0°$	0·345	$33\text{-}80°$	0·535
Benzene . . .	$5\cdot4°$	0·2032	$6°$	0·3350
$CCl_3 . CH(OH)_2$.	$17\text{-}44°$	0·206	$51\text{-}88°$	0·470
Naphthalene . . .	$60\text{-}70°$	0·334	$80°$	0·396
Nitronaphthalene .	$40\text{-}45°$	0·274	$56\text{-}60°$	0·360
Thymol	$50°$	0·462	$50°$	0·566

In most cases the rise on passing to the liquid state is too large to be accounted for by the ordinary effect of temperature. Moreover, Timofejew[1] has pointed out that the temperature coefficient for highly associated compounds is considerably larger than that for unassociated. A few substances are contrasted in Table IV.

§ 3. *DENSITY AND SPECIFIC HEAT*

Boltzmann[2] and Richarz[3] have contributed to the kinetic theory of solids. The former proved, in a manner too com-

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[1] *Chem. Centralblatt,* **2,** 429 (1905).

[2] *Sitzungsberichte der Wiener Akad.,* **63,** [2] 731 (1871).

[3] *Wied. Ann.,* **48,** 708 (1893); **67,** 704 (1899); *Naturwissenschaftliche Rundschau,* **15,** 221 (1900); **9,** 221, 237 (1894); also *Zeitsch. anorg. Chemie;* also Streintz, *Drude's Ann.,* **8,** 847 (1902).

plicated to be shown here, that about half the heat which is absorbed by a solid is employed in performing internal work. The work of Richarz is especially interesting, since it has shown that the atomic heat of the solid elements may be deduced from the kinetic theory. When an element is heated, work is spent not only in raising the mean kinetic energy of the atoms (Q_k), but also in overcoming attractive forces (Q_m), that is, in moving the atoms out of the position of equilibrium. It can be shown from Clausius' " virial " law that if the distance through which an atom is moved be small compared with the space between them, the work done in moving the atom is approximately equal to that expended in increasing the kinetic energy. This, it will be noticed, is similar to the conclusion formed by Boltzmann. Now, on heating a monatomic gas at constant volume, the work done against the cohesion of the atoms is very small, all the heat supplied is used in increasing the kinetic energy of the gas. The atomic heat of monatomic gases at constant volume is about 3, hence that of the solid elements must be approximately $3 + 3$ or 6. This conclusion agrees with Dulong and Petit's law that the atomic heat of the elements is constant and about equal to the above number.

TABLE IV.

Substance.	C_{20}.	$\dfrac{dc}{dt}$	Substance.	C_{20}.	$\dfrac{dc}{dt}$
Heptane . . .	0·490	0·0010	Methyl alcohol .	0·600	0·0016
Chloroform . .	0·234	0·0001	Ethyl alcohol .	0·593	0·0024
Carbon tetra-			Propyl alcohol .	0·579	0·0024
chloride . .	0·207	0·00018	Isobutyl alcohol.	0·579	0·0021
Aniline . . .	0·491	0·0004	Isoamyl alcohol .	0·554	0·0024
Pyridine . . .	0·405	0·0006	Acetic acid . .	0·487	0·0014
Ethyl acetate .	0·478	0·001			

Richarz also showed that the exceptions to Dulong and Petit's law can be explained. In the above theory two assumptions are made, neither of which is strictly accurate.

1. That no external work is performed on heating the substance.

2. That the distance between the atoms is very large compared to the displacement of each atom.

With regard to the first assumption, the substance when heated expands, and thus a certain amount of heat disappears in doing work against external pressure, but it is so small that the error caused by neglecting it is covered by those of experiment. To illustrate this we may take the case of copper.[1] On heating one gram of this substance through one degree centigrade, o·ooooooi5 heat unit is expended on external work, whilst the total amount spent in raising the temperature is about o·094 unit.

The errors from the second source are by far the larger, and it is evident that they will be greatest when the atomic volume and atomic weight of the element are small. With small atomic volume the space between the atoms is reduced, whilst with small atomic weight the atomic displacement will be greater for a given amount of energy than with heavier atoms. Thus in such an element the interatomic space and the atomic displacement tend to approach one another in magnitude, and consequently the atomic heat must differ from the normal value. Experiment confirms this conclusion. The greatest difference between the atomic heat of experiment and the theoretical value is found with elements of low atomic weight and volume; and the values obtained with these in experiment are always too low. The data in support of this are given in Table V.

Wigand[2] extended these ideas to the allotropic forms of the elements. The modification which possesses the smallest atomic volume (greatest specific gravity) must also have the lowest specific heat. The data collected in Table V. show that practice again supports the theory.

Behn[3] discovered that at low temperatures the elements

[1] Winkelmann, *Handbuch der Physik, Wärme.*, p. 188 (1906).

[2] *Drude's Ann.*, [4] **22**, 64–98 (1907); see Bettendorf and Wullner, *Pogg. Ann.*, **133**, 293 (1868), for other measurements of specific heat of allotropic forms.

[3] *Wied. Ann.*, **66**, 225 (1898); see also Tilden, *Proc. Roy. Soc.*, **66**, 244 (1900); and Dewar, *ibid.*, **76**, 325 (1905), for other measurements of specific heat at low temperatures.

with small atomic weight when cooled decrease in specific heat more rapidly than those of higher atomic weight.   Richarz

TABLE V.

Substance.	Modification.	Sp. gr.	Sp. heat.	Temp. of estimation.
Carbon	Diamond . . .	3·518	0·1128	10·7°
,, ...	Graphite . . .	2·25	0·1604	10·8°
,, ...	Gas-carbon . .	1·885	0·2040	24·68°
,, ...	Crystalline . .	2·535	0·2518	0–100°
Boron	Amorphous . .	2·45	0·3066	0–100°
,, ...	Crystalline . .	2·49	0·165	21°
Phosphorus . . .	Red	2·296	0·1829	0–51°
,, ...	Yellow	1·828	0·202	13–36°
Sulphur	Rhombic . . .	2·06	0·1728	0–54°
,, ...	Monoclinic . .	1·96	0·1809	0–52°
,, ...	Insol. amorphous	1·89	0·1902	0–53°
,, ...	Sol. amorphous .	1·86	0·2483	0–50°
Arsenic	Grey	5·87	0·0822	0–100°
,, ...	Black	4·78	0·0861	0–100°
Selenium . . .	Crystalline . .	4·8	0·0840	22–62°
,, ...	Amorphous . .	4·3	0·1125	21–57°
Tellurium . . .	Crystalline . .	6·3	0·0483	15–100°
,, ...	Amorphous . .	6·0	0·0525	15–100°
Tin	White	7·3	0·0542	0–21°
,, ...	Grey	5·85	0·0589	0–18°

claims that this further supports his theory.   Some of Regnault's [1] measurements may also be quoted to show the effect of density on specific heat.

Substance.	Density.	Sp. heat.
Steel, soft	7·8609	0·1165
Steel, hard	7·7982	0·1175
Copper soft	?	0·0950
Copper, hammered .	?	0·0936

In this connection notice should be taken of de Heen's very interesting attempt to show that the internal work performed is equal in substances of a similar chemical nature.   De Heen

[1] *Ann. Chim. Phys.*, [3] 9, 322 (1843).

adopts Clausius' idea that the "true" specific heat is the same for all atoms. The specific heat of hydrogen at constant volume is 2·4, and this is chosen as the unit of atomic heat. The molecular heat of a substance will therefore be the sum of the true atomic heats and the heat spent in doing internal work. Thus we have—

$$M.C. = n \times 2·4 + Q_m$$

where M is the molecular weight, and n the number of atoms in the molecule. De Heen finds the values of Q_m calculated in this way are fairly constant in each class of substance. A few examples are quoted.[1]

TABLE VI.

Substance.	M. C.	Q_m.	Substance.	M. C.	Q_m.
Methyl acetate . .	37·5	11·2	Isobutyric acid . .	44·37	10·8
Ethyl acetate . . .	43·7	10·1	Isovalerianic acid .	51·5	10·7
Propyl acetate . . .	51·0	9·8	Phenetole	57·95	12·3
Amyl acetate . . .	67·1	11·7	Phenyl propyl ether.	64·74	11·9
Capryl acetate . . .	88·8	12·6	Anisole	48·9	10·5
Formic acid . . .	24·4	12·4	Cresyl methyl ether	55·06	9·46
Acetic acid	30·9	11·7	Cresyl ethyl ether .	64·74	12·07
Propionic acid . . .	38·1	11·7	Xylenyl methyl ether	63·24	10·4
Butyric acid . . .	45·1	11·5			

§ 4. *SPECIFIC HEAT OF INORGANIC SUBSTANCES*[2]

1. *Elements.*—The law of Dulong and Petit.

In 1819 Dulong and Petit[3] found that the product of the specific heat and atomic weight (atomic heat) was almost the same with different elements, and they concluded that all atoms have the same heat capacity. Since the determinations

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[1] *Essai de Physique Comparée*, Brussels (1883), or Ostwald, *Lehrbuch Allgm. Chemie*, 2nd. ed., I. 586 (1891); and de Heen, *Bull. Acad. Belg.*, [3] **12**, 416 (1886).

[2] The specific heats of gases are not dealt with here ; they are considered in *Stoichiometry*, this series, Young (1908).

[3] *Ann. Chim. Phys.*, [2] **10**, 395 (1819).

TABLE VII.

ATOMIC AND SPECIFIC HEATS OF THE ELEMENTS.

Element	At. heat.	Sp. heat.	Temperature of observation.	Element	At. heat.	Sp. heat.	Temperature of observation.
Lithium	6·5	0·9408	27–99°	Selenium (cryst.)	6·6	0·084	22–62°
Beryllium	4·6	0·506	0–300°	Zirconium	6·0	0·0660	0–100°
Boron (cryst.) 1.	2·1	0·1915	–39·6°	Molybdenum	6·3	0·0659	5–75°
2.	4·0	0·3363	233°	Ruthenium	6·2	0·0611	0–100°
Carbon (cryst.) 1.	0·76	0·0635	–50·5°	Rhodium	6·0	0·0580	10–97°
2.	5·5	0·459	985°	Palladium	6·3	0·0592	0–100°
Sodium	6·5	0·283	–78—+17°	Silver	6·0	0·0559	0–100°
Magnesium	6·1	0·251	75°	Cadmium	6·2	0·0548	0–100°
Aluminium	6·4	0·2356	15–435°	Indium	6·5	0·0569	0–110°
Silicon (cryst.) 1.	3·9	0·1360	–39·8°	Tin	6·6	0·0559	0–100°
2.	5·8	0·203	23°	Antimony	6·1	0·0508	17–92°
Phosphorus	5·5	0·1788	–21—+7°	Iodine	6·0	0·0541	9–98°
Sulphur	5·7	0·1764	15–97°	Tellurium	6·7	0·0525	15–100°
Potassium	6·5	0·1662	–78—+23°	Caesium	6·4	0·0481	0–20°
Calcium	7·2	0·1804	0–100°	Lanthanum	6·2	0·0448	0–100°
Titanium	6·2	0·1288	0–211°	Cerium	6·3	0·0448	0–100°
Vanadium	5·9	0·1153	0–100°	Tungsten	6·2	0·0336	0–100°
Chromium	6·3	0·1208	0–100°	Osmium	5·9	0·0311	19–98°
Manganese	6·7	0·1217	14–97°	Iridium	6·2	0·0323	0–100°
Iron	6·5	0·1162	23–100°	Platinum	6·3	0·0323	0–100°
Nickel	6·4	0·109	18–100°	Gold	6·2	0·0316	0–100°
Cobalt	6·3	0·1067	9–97°	Mercury	6·4	0·0319	–78—–40°
Copper	6·0	0·0936	20–100°	Thallium	6·7	0·0326	20–100°
Zinc	6·1	0·0935	0–100°	Lead	6·4	0·0310	18–100°
Gallium	5·6	0·0802	to 119°	Bismuth	6·3	0·0304	17–99°
Germanium	5·6	0·0773	0–200°	Thorium	6·4	0·02757	0–100°
Arsenic (cryst.)	6·2	0·083	21–68°	Uranium	6·7	0·0280	0–98°

of Dulong and Petit were made with only thirteen elements, some of which were evidently impure, further investigation was necessary to place the law on a firm basis. The chief advances in this direction were successively made by Regnault[1] and by Kopp.[2] Without describing the important part which the law has played in the acceptance of the present atomic weights, we may say that later investigation, while confirming it in general outline, has shown it to be only approximately true. The table which is appended (No. VII.) shows the specific and atomic heats of most of the elements.

It will be seen that the atomic heat is only approximately constant. With the majority of the elements the value lies near 6, and as a rule a little above it. Taking the average of all but the exceptional cases of beryllium, carbon, boron, and silicon, the atomic heat of an element may be said to be about 6·3. It should be noticed that the greater differences from this normal value are shown by elements of low atomic weight. For some time carbon, silicon, and boron were regarded as anomalies, but Weber's researches[3] showed that they may be brought into line with the other elements if their specific heat is measured at sufficiently high temperature. Weber's interesting data are quoted in Table VIII.

It is worth noting that Dewar[4] found the specific heat of diamond at the interval $-188°$ to $-252°$ to be as low as 0·0043.

Rising from low temperatures, the specific heat alters very rapidly; but at higher temperatures it tends to become constant, and finally the atomic heat would no doubt approach the normal value of 6. From these measurements it is also clear that the choice of a correct temperature of comparison is very important. No doubt boron, silicon and carbon are peculiarly subject to the influence of temperature, but all the other elements are similarly affected, though in a less degree. We

[1] *Ann. Chim. Phys.*, [2] 73, 5 (1840).

[2] *Ann. Suppl.*, 8, 1, 289 (1864).

[3] *Ber.*, 5, 303 (1872); *Jahresberichte für Chemie*, 1874, 64; see also Dewar, *Phil. Mag.*, [4] 44, 461 (1872).

[4] *Proc. Roy. Soc.*, 76, 325 (1905).

cannot, therefore, form an estimate of the accuracy of the law until the temperature effect is eliminated, and as yet this has not been successfully attempted.

TABLE VIII.

Substance.	Temperature.	Sp. heat.	Atomic heat.
Diamond	$-50 \cdot 5°$	0·0635	0·76
,, ...	$-10 \cdot 6°$	0·0955	1·1
,, ...	$+10 \cdot 7°$	0·1128	1·3
,, ...	$33 \cdot 4°$	0·1318	1·6
,, ...	$58 \cdot 3°$	0·1532	1·8
,, ...	$85 \cdot 5°$	0·1765	2·1
,, ...	$140 \cdot 0°$	0·2218	2·6
,, ...	$206 \cdot 1°$	0·2733	3·3
,, ...	$247 \cdot 6°$	0·3026	3·6
,, ...	$606 \cdot 7°$	0·4408	5·3
,, ...	$806 \cdot 5°$	0·4489	5·4
,, ...	$985 \cdot 0°$	0·4589	5·5
Boron (crystalline) [1] . .	$-39 \cdot 6°$	0·1915	2·1
,, ,, . .	$+26 \cdot 6°$	0·2382	2·6
,, ,, . .	$125 \cdot 8°$	0·3069	3·4
,, ,, . .	$177 \cdot 2°$	0·3378	3·7
,, ,, . .	$233 \cdot 2°$	0·3663	4·0
Silicon (crystalline) . .	$-39 \cdot 8°$	0·1360	3·9
,, ,, . .	$21 \cdot 6°$	0·1697	4·8
,, ,, . .	$138 \cdot 7°$	0·1964	5·6
,, ,, . .	$184 \cdot 3°$	0·2011	5·71
,, ,, . .	$232 \cdot 4°$	0·2029	5·76

But apart from these considerations, there are others which render it almost certain that the law is only approximately true. From what has been already said of the specific heat of solids, it is clear that unless the heat spent in doing internal work is the same for each element their atomic heats cannot be equal. It will be recalled that Richarz has shown that the internal work, and consequently the atomic heat, is less with elements of small atomic weight and volume.

2. *Compounds.*—The laws of Neumann and of Kopp.— When Dulong and Petit's law had been accepted, research was extended to the elements in the combined state. It was

[1] Moissan and Gautier have also determined the influence of temperature on the specific heat of boron, *Ann. Chim. Phys.*, [7] 7, 568 (1896).

Neumann,[1] in 1831, who first discovered a relation between specific heat and composition. The law which he framed may be shortly stated as follows, in a form altered to suit modern ideas :—

"Substances of similar chemical composition and structure have the same molecular heat."

Some of the data on which this was based are quoted in the appended list.

<div align="center">TABLE IX.</div>

Substance.	Formula.	Specific heat.	Mol. heat.
Heavy spar	$BaSO_4$	0·1068	24·9
Anhydrite	$CaSO_4$	0·1854	25·2
Celestine	$SrSO_4$	0·130	23·87
Calcspar	$CaCO_3$	0·204	20·4
Magnesite	$MgCO_3$	0·227	19·1
Spathic iron ore . . .	$FeCO_3$	0·182	21·1
Calamine	$ZnCO_3$	0·171	21·4
Zinc blende	ZnS	0·112	10·9
Cinnabar	HgS	0·052	12·0
Realgar	As_2S_2	0·130	13·9 × 2
Galena	PbS	0·053	12·6
Magnesia	MgO	0·276	11·1
Mercuric oxide . . .	HgO	0·049	10·6
Zinc oxide	ZnO	0·132	10·7
Cupric oxide	CuO	0·137	10·9

The agreement between the molecular heats is not very close, but seeing that most of the substances investigated were minerals, and consequently impure, the differences are not surprising. Regnault's[2] measurements were more accurate, and they were made with purer substances. He investigated a large number of compounds, chiefly oxides, halides, sulphides, carbonates, sulphates, and nitrates; and the results fully confirmed the law stated by Neumann. The data from the oxides of the formula RO are given in detail in Table X.

Joule, in 1844,[3] and Woestyn,[4] some four years later,

[1] *Pogg. Ann.*, **23**, 32 (1831).

[2] *Ann. Chim. Phys.*, [3] 1, 129 (1841) ; *Pogg. Ann.*, **53**, 60, 243 (1841).

[3] *Phil. Mag.*, [3] **25**, 334 (1844).

[4] *Ann. Chim. Phys.*, [3] **23**, 295 (1848).

asserted that the molecular heat of a compound is equal to the sum of the atomic heats of the atoms which compose it. Thus, for example, the molecular heat of a sulphide whose formula is RS_2 would be equal to the sum of the atomic heat of R and twice the atomic heat of sulphur. The researches of Kopp[1] have done more to establish this law than any others, and therefore his name is usually associated with it.

TABLE X.

Substance.	M. wt.	Sp. heat.	Mol. heat.
Lead oxide, PbO . .	222·9	0·0512	11·4
Copper oxide, CuO . .	63·6	0·1420	11·3
Magnesia, MgO . . .	40·4	0·2439	9·8
Manganous oxide, MnO	71·0	0·1570	11·1
Nickel oxide, NiO . .	74·7	0·1588	11·9
Mercuric oxide, HgO .	216·3	0·0518	11·2
Zinc oxide, ZnO . . .	81·4	0·1248	10·26

Neumann, as we have seen, pointed out that the molecular heats of the members in one class of compounds are approximately constant. The mean value of these may be called the average molecular heat of the particular type of substance. Now, Kopp showed that if this molecular heat be divided by the number of atoms in the compound, a value is obtained which is usually very near to the average atomic heat, 6·4. This is illustrated by Table XI.

The first of these tables shows the approximate equality of the molecular heats of compounds in the same class, whilst the second table gives in the right-hand column the average atomic heat calculated from the molecular heat.

Some compounds, however, give for the average atomic heat values which are considerably smaller than 6; and all these contain elements which do not obey Dulong and Petit's law: boron, carbon, silicon, phosphorus, sulphur, oxygen, nitrogen, hydrogen, or fluorine. Of these elements, the first five are known to have low atomic heats in the

[1] *Ann. Suppl.*, **3**, I. 289 (1864).

TABLE XI.

CHLORIDES RCl. Average molecular heat = 12·8.			CHLORIDES RCl$_2$. Average molecular heat = 18·5.		
Substance.	Spec. heat.	Mol. heat.	Substance.	Spec. heat.	Mol. heat.
AgCl . . .	0·0911	13·1	BaCl$_2$ . .	0·902	18·8
CuCl . . .	0·1383	13·7	CaCl$_2$ . .	0·1642	18·2
HgCl . . .	0·0520	12·3	HgCl$_2$ . .	0·0689	18·7
KCl . . .	0·1730	12·9	MgCl$_2$ . .	0·1946	18·5
LiCl . . .	0·2821	12·0	MnCl$_2$ . .	0·1425	17·9
NaCl . . .	0·2140	12·5	PbCl$_2$ . .	0·0664	18·5
RbCl . . .	0·112	13·5	SnCl$_2$ . .	0·1016	19·3
			SrCl$_2$ . .	0·1199	19·0
			ZnCl$_2$ . .	0·1362	18·6

IODIDES RI$_2$.

Average molecular heat = 19·4.

HgI$_2$ . . .	0·0420	19·1
PbI$_2$ . . .	0·0427	19·7

IODIDES RI.

Average molecular heat = 13·4.

AgI . . .	0·0616	14·5
CuI . . .	0·0687	13·1
HgI . . .	0·0395	12·9
KI . . .	0·0819	13·6
NaI . . .	0·0868	13·0

DOUBLE CHLORIDES R′$_2$RCl$_6$.

Average molecular heat = 54·8.

K$_2$SnCl$_6$ . . .	0·133	54·5
K$_2$PtCl$_6$ . . .	0·113	54·9

TABLE XII.

Empirical formula.	Average mol. heat.	No. of atoms . n.	Mol. heat $\dfrac{}{n}$
RCl . . .	12·8	2	6·4
RCl$_2$ . . .	18·5	3	6·2
R′$_2$RCl$_6$ . .	54·8	9	6·1
RI	13·4	2	6·7
RI$_2$. . . .	19·4	3	6·5
RBr . . .	13·9	2	6·8
RBr$_2$ . . .	19·6	3	6·5

uncombined state, whilst the others may be suspected of this, since they are of low atomic weight. Some examples follow.

TABLE XIII.

Type.	Av.mol.heat.	Av. at. heat.	Type.	Av.mol.heat.	Av. at. heat.
RO	11·1	5·6	RCO$_3$ . . .	20·7	4·1
R$_2$O$_3$. . . .	27·2	5·4	RSO$_4$ . . .	26·1	4·3
RO$_2$	13·7	4·6	RSiO$_3$ . .	20·5	4·1
RO$_3$	18·8	4·7	RNO$_3$ . .	23·0	4·6
RS	11·9	5·9	RN$_2$O$_6$. .	38·1	4·2
R$_2$S	18·8	6·2	B$_2$O$_3$ . .	16·6	3·3
KClO$_3$ . .	24·8	4·9	SiO$_2$. . .	11·3	3·8
KClO$_4$ . .	26·3	4·4	H$_2$O. . .	8·6	2·9

Hence Kopp concluded that the atomic heats of the elements are approximately the same, whether free or in combination with one another. Additional support is lent to this conclusion by the facts that—

1. The molecular heats of compounds which contain an equal proportion of the same abnormal element are approximately equal; where the proportion of the abnormal element is greater, the divergence of the average atomic heat from the normal value is also greater. Thus, in the following series the molecular heats are about 27 :—

$$R : O = 2 : 4$$

R$_2$O$_4$	27·4
CaWO$_4$	27·9
KClO$_4$	26·3
KMnO$_4$	28·3

and in the next the average atomic heat decreases with increasing proportion of oxygen :—

Type.	Average atom. heat.
R$_2$O$_2$	5·6
R$_2$O$_3$	5·4
R$_2$O$_4$	4·6
R$_2$O$_6$	4·7

2. That the atomic heats of the abnormal elements obtained by calculation from their compounds are almost the

same as their atomic heats in the free state. For example, take sulphur as calculated from the sulphides RS. The latter substances have the average molecular heat 11·9, and subtracting from this the value of R = 6·4, we obtain for combined sulphur 5·5. The atomic heat of the element lies between 5·2–5·6, according to its temperature and condition.

From his calculations Kopp found that the following elements were " normal " :—

Ag, Al, As, Au, Ba, Bi, Br, Ca, Co, Cr, Cu, Fe, Hg, I, Ir, K, Li, Mg, Mn, Mo, Na, Ni, Os, Pb, Pd, Pt, Rb, Rh, Sb, Se, Sn, Sr, Te, Th, Ti, W, Zn, Zr.

The abnormal elements had the following values :—

$$C = 1·8, \; H = 2·3, \; B = 2·7, \; Si = 3·8, \; O = 4·0, \; F = 5·0,$$
$$P = 5·4, \; S = 5·4.$$

Water of crystallisation gave the molecular heat = 8, which is almost the same value as that of ice (8·3).

Most of Kopp's measurements were made between the ordinary temperature and 50° C. ; but Tilden [1] has shown that the law still holds at low temperatures. The data which he obtained with nickel telluride are quoted in illustration :—

Nickel Telluride.	Absolute Temperature.						
	100°	200°	300°	400°	500°	600°	700°
Molecular heat . . .	9·2	11·08	12·22	13·0	13·49	13·85	14·11
Sum of atomic heats .	8·38	11·35	12·41	12·92	13·15	13·28	13·35

Before leaving this subject it should be noticed that both Neumann's and Kopp's laws are only approximately true ; nevertheless they clearly illustrate the additive character of specific heat. If the measurements were sufficiently accurate and if they were made at corresponding temperatures for each substance, we should no doubt be able to discover constitutive

[1] *Proc. Roy. Soc.*, **73**, 226 (1904).

relations ; but in the comparatively simple inorganic com-
pounds which we have examined, the additive character of
specific heat is far more prominent than with organic sub-
stances.   In these we shall find the influence of constitution
more marked.

§ 5. *ORGANIC COMPOUNDS*

Liquids.—Since the effect of temperature on the specific heat
of liquids is fairly large, the choice of a correct temperature of
comparison is necessary.   The plan recommended by Schiff[1]
is undoubtedly the best.   It consists in comparing the specific
heats at temperatures which are equal fractions of the critical
temperatures, when according to the theory of J. van der
Waals, the liquids should be in "corresponding" states.   Most
observers have compared the specific heats over a particular
range of temperature to which they have adhered throughout
their work ; but unfortunately the range of temperature chosen
has not been the same in every case, and for this reason it is
almost useless to compare data from different sources.
Sufficient material, however, can be collected to show the
general nature of the specific heat of organic compounds.

Before examining the data it is appropriate to discuss the
influence of temperature on the specific heat of liquids.
Schiff's work on the subject is the only one of importance, and
reference has already been made to it on a previous page.   He
found that the average specific heat of a substance over an
interval t–t' may be represented as

$$C_{(t-t')} = A + b(t-t')$$

or the true specific heat at any temperature

$$C_t = A + 2bt$$

From about ninety compounds he showed that the value of
b is the same for substances of a similar chemical nature ; only
one exception was met with, namely, formic acid.   The results
are collected in the following table, which shows both constants
A and b.

[1] *Ann.*, **234**, 300, 331 (1886) ; *Zeit. Phys. Chem.*, **1**, 376 (1887).

TABLE XIV.

Substance.	$C = \Lambda + 2bt.$
Alkyl esters of monobasic fatty acids	$0.4416 + 0.0_388t$
Allyl acetate . . . . ⎫	
Allyl isobutyrate . . . ⎬	$0.4305 + 0.0_388t$
Allyl propionate . . . ⎫	
Allyl butyrate . . . . ⎬	$0.4330 + 0.0_388t$
Allyl valerate . . . . ⎭	
Ethyl oxalate . . . . ⎫	
Propyl oxalate . . . . ⎪	
Ethyl malonate . . . ⎬	$0.4199 + 0.0_366t$
Propyl malonate . . . ⎭	
Allyl oxalate	$0.4122 + 0.0_366t$
Isobutyl oxalate	$0.2274 + 0.0_366t$
Methyl benzoate	$0.363 \ + 0.0_375t$
Ethyl benzoate	$0.374 \ + 0.0_375t$
Propyl benzoate	$0.383 \ + 0.0_375t$
Allyl benzoate	$0.373 \ + 0.0_375t$
Methyl chloracetate . . .	$0.3747 + 0.0_338t$
Ethyl chloracetate. . . .	$0.390 \ + 0.0_338t$
Propyl chloracetate . . .	$0.4067 + 0.0_338t$
Allyl chloracetate	$0.3888 + 0.0_338t$
Methyl dichloracetate . .	$0.3032 + 0.0_338t$
Ethyl dichloracetate . . .	$0.3215 + 0.0_338t$
Propyl dichloracetate . . .	$0.3335 + 0.0_338t$
Allyl dichloracetate . . .	$0.3244 + 0.0_338t$
Methyl trichloracetate . .	$0.2592 + 0.0_338t$
Ethyl trichloracetate . . .	$0.2778 + 0.0_338t$
Propyl trichloracetate . .	$0.2892 + 0.0_338t$
Allyl trichloracetate . . .	$0.2806 + 0.0_338t$
Benzene . . . . . ⎫	
Toluene . . . . . ⎪	
m. Xylene . . . . . ⎬	$0.3834 + 0.0_21043t$
p. Xylene . . . . . ⎪	
Ethyl benzene . . . . ⎭	
Pseudo cumene . . . ⎫	
Mesitylene . . . . . ⎬	$0.3929 + 0.0_21043t$
Propyl benzene . . . ⎫	
Cymene. . . . . . ⎬	$0.4000 + 0.0_21043t$
Anisole . . . . . ⎫	
Methyl cresyl ether . . ⎬	$0.405 \ + 0.0_386t$
Methyl xylenyl ether . . .	$0.417 \ + 0.0_386t$
Phenetole . . . . . ⎫	
Propyl phenyl ether . . ⎬	$0.4288 + 0.0_386t$
Ethyl cresyl ether . . . ⎭	
Acetic acid . . . . ⎫	
Propionic acid . . . . ⎬	$0.444 \ + 0.0_21418t$
Butyric acid . . . . ⎭	
Isobutyric acid . . . ⎫	
Valerianic acid. . . . ⎬	$0.4352 + 0.0_21418t$
Formic acid	$0.4966 + 0.0_2709t$
Isoamyl alcohol	$0.5012 + 0.0_227t$

It seems then that the specific heat of organic liquids, like that of most metals, is a linear function [1] of the temperature.

TABLE XV.

ISOMERS OF SIMILAR STRUCTURE.

Substance.	Sp. ht.	Temp. of observation.	Mol. ht.	Formula.
Butyric acid	0·5152	20–100° [2]	45·34	$C_4H_8O_2$
Isobutyric acid	0·5146	,,	45·28	
Propaldehyde	0·5794	,,	33·6	C_3H_6O
Acetone	0·5706	,,	33·1	
Butyryl chloride . . .	0·3983	,,	42·2	C_4H_7OCl
Isobutyryl chloride . . .	0·3911	,,	41·4	
Propyl bromide	0·2560	,,	31·5	C_3H_7Br
Isopropyl bromide . . .	0·2580	,,	31·7	
Propyl acetate	0·4880	,,	49·8	$C_5H_{10}O$
Isovalerianic acid . . .	0·5000	,,	51·0	
p. Xylylene dibromide. .	0·180	15–60° [3]	47·5	$C_8H_8Br_2$
o. Xylylene dibromide .	0·183	,,	48·3	
m. Xylylene dibromide .	0·184	,,	48·5	
p. Xylylidene tetrachloride	0·242	,,	59·0	$C_8H_6Cl_4$
o. Xylylidene tetrachloride	0·240	,,	58·5	

ISOMERS OF DIFFERENT STRUCTURE.

Allyl alcohol	0·6441	20–100° [2]	37·35	C_3H_6O
Propaldehyde	0·5794	,,	33·6	
Propyl oxalate	0·4503	10·1–82° [4]	78·3	$C_8H_{14}O_4$
Ethyl succinate	0·4696	10·0–82·2°	81·7	
Isobutyl oxalate	0·4570	88–82°	92·3	$C_{10}H_{18}O_4$
Propyl succinate . . .	0·4676	9–83°	94·4	
Isoamyl oxalate	0·4637	9·3–81·5°	106·6	$C_{12}H_{22}O_4$
Isobutyl succinate . . .	0·4721	9·8–82·1°	108·5	
Chlorotoluene	0·3480	8·7–81·5°	43·8	C_7H_7Cl
Benzyl chloride	0·3555	7·3–81·6°	44·7	
Methyl cresyl ether . .	0·4914	*	59·9	C_8H_{18}
Phenetole	0·5148	*	62·8	

* Calculated for 100° from $C_t = A + Bt$.

In the following pages the molecular heats are compared,

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[1] Aniline is exceptional, see Kurbatow, *Journ. Russ. Phys. Chem. Soc.*, **34**, 119; **35**, 766 (1902).

[2] Von Reis, *Wied. Ann.*, **13**, 447 (1881).

[3] Colson, *Comptes Rend.*, **104**, 428 (1887).

[4] Schiff, *Zeit. Phys. Chem.*, **1**, 376 (1887).

that is, the quantities of heat required to raise one gram-molecule of each substance through one degree centigrade; the numbers were obtained by multiplying the molecular weight by the specific heat.

Isomers.—The study of isomeric compounds makes evident both the additive and constitutive nature of molecular heat. Isomers of similar structure have almost identical molecular heats, whilst those of different structure have different molecular heats.   Von Reis [1] was the first to draw attention to this, and his conclusions are, on the whole, borne out by later observations. Some illustrations are presented in Table XV.

The above comparisons are made at arbitrary temperatures, but the same results are obtained when "corresponding" temperatures are adopted.

TABLE XVI.

Substance.	T o·6 of abs. crit. temp.	Specific heat at T.	Molecular heat.
Methyl valerate . . .	69·6	0·5028	58·3⟩
Ethyl butyrate	71·4	0·5044	58·4
Propyl propionate . . .	73·8	0·5065	58·7⟩
Isobutyl acetate . . .	70·2	0·5034	58·4
Isoamyl formate . . .	74·4	0·5070	58·7⟩
Ethyl valerate	80·7	0·5126	66·6
Propyl isobutyrate . . ·.	81·0	0·5129	66·6⟩
Propyl butyrate . . .	86·4	0·5177	67·3
Isobutyl propionate. . .	82·2	0·5139	66·9⟩
Isoamyl acetate . . .	85·2	0·5165	67·2

Relations between molecular heat and special types of isomerism are almost entirely wanting.   The only attempt in this direction is that of Mabery and Goldstein,[2] who inferred from the comparison of *iso*heptane with *n*. heptane and of *iso*decane with *n*. decane, that branching of the carbon chain influences molecular heat.   This is probably true, but whether it can be legitimately deduced from their measurements is doubtful.   A more convincing case is that of the butyl alcohols,

[1] *Wied. Ann.*, **13**, 447 (1881).
[2] *Amer. Chem. Journ.*, **28**, 66 (1902).

whose molecular heats are contrasted in the list below. The specific heat of trimethyl carbinol would no doubt be considerably higher if measured over the same interval as the other alcohols. Two other instances are added in which the molecular heats at the boiling-points are compared.

TABLE XVIA.

Substance.	Specific heat.	Measured at	Mol. heat.
Isoheptane	0·5005	0–50°	50·0
n. Heptane	0·5074	0–50°	50·7
Isodecane	0·4951	0–50°	70·3
n. Decane . . .	0·5021	0–50°	71·3
n. Butyric acid . .	0·6751	163° (B.P.)	59·3
Isobutyric acid . .	0·6637	155° (B.P.)	58·3
n. Butyl alcohol . .	0·689 [1]	20–114°	51·0
Isobutyl alcohol . .	0·716 [1]	21–119°	53·0
Trimethyl carbinol . .	0·722 [2]	25–45°	53·4
Allyl *n.* butyrate . .	0·5588	143° (B.P.)	71·5
Allyl isobutyrate . .	0·5484	134° (B.P.)	70·2

Homologues.—The figures given in the appended list to illustrate the molecular heats of homologous series are drawn from four sources: the observations of von Reis,[3] de Heen,[4] Schiff,[5] and Mabery and Goldstein.[6] On inspecting the table it will be seen that additional CH_2 causes an increase in molecular heat which is fairly constant throughout any given series. It is, however, uncertain whether the homologous increment is the same for all series. In four of the series the comparison is made at the boiling-point, and throughout these it seems that the value of CH_2 is approximately constant, but the data are too few to give any weight to the conclusion. In homologues, then, the additive nature of molecular heat stands out clearly.

Schiff found that the specific heats of all the fatty esters are

[1] Longuinine, *Ann. Chim. Phys.*, [7] 13, 289 (1898).
[2] De Forcrand, *Comptes Rend.*, 136, 1034 (1903).
[3] *Wied. Ann.*, 13, 447 (1881).
[4] *Essai de physique comparée*, Brussels (1883).
[5] *Ann.*, 234, 300 (1886); and *Zeit. Phys. Chem.*, 1, 376 (1887).
[6] *Amer. Chem. Journ.*, 28, 66 (1902).

TABLE XVII.

NORMAL HYDROCARBONS.

Sp. heat measured at 0-50° C.

Substance.	Specific heat.	Mol. heat.	Diff.	Substance.	Specific heat.	Mol. heat.	Diff.
C_6H_{14}	0·5272	45·3	5·4	$C_{11}H_{24}$ . . .	0·5013	78·1	6.9
C_7H_{16}	0·5074	50·7	6·8	$C_{12}H_{26}$ . . .	0·4997	85·0	6·6
C_8H_{18}	0·5052	57·5	6·9	$C_{13}H_{28}$ . . .	0·4986	91·6	6·9
C_9H_{20}	0·5034	64·4	6·9	$C_{14}H_{30}$ . . .	0·4973	98·5	6·8
$C_{10}H_{22}$	0·5021	71·3	6·8	$C_{15}H_{32}$ . . .	0·4966	105·3	6·7
$C_{11}H_{24}$	0·5013	78·1		$C_{16}H_{34}$ . . .	0·4957	112·0	

NORMAL ALCOHOLS.

Sp. heat measured at 20°-boiling-point.

Substance	Specific heat	Mol. heat	Diff.	Substance	Specific heat	Mol. heat	Diff.
CH_3OH . . .	0·6544	20·9	9·4	C_4H_9OH . .	0·6873	50·9	9·6
C_2H_5OH . . .	0·6587	30·3	10·2	$C_6H_{11}OH$ . .	0·6877	60·5	
C_3H_7OH . . .	0·6748	40·5	10·4	$C_8H_{17}OH$ . .	0·6876	89·4	3×9·6
C_4H_9OH . . .	0·6873	50·9					

Sp. heat measured at 10-50°.

Substance		Mol. heat	Diff.	Substance		Mol. heat	Diff.
CH_3OH . . .	—	21·6	8·3	C_4H_9OH . .	—	47·0	8·5
C_2H_5OH . . .	—	29·9	9·7	$C_6H_{11}OH$ . .	—	55·5	
C_3H_7OH . . .	—	39·6	7·4	$C_8H_{17}OH$ . .	—	76·8	3×7·1
C_4H_9OH . . .	—	47·0					

ESTERS OF FATTY ACIDS.

Sp. heat at boiling-point calculated from $C = 0·4416 + 0·0_288t$.

Substance	Specific heat	Mol. heat	Diff.	Substance	Specific heat	Mol. heat	Diff.
$C_2H_5COOCH_3$.	0·5115	45·0	8·9	$C_2H_5COOC_4H_9$	0·5621	73·0	10·8
$C_2H_5COOC_2H_5$	0·5285	53·9	9·7	$C_2H_5COOC_5H_{11}$	0·5824	83·8	10·7
$C_2H_5COOC_3H_7$	0·5488	63·6	9·4	$C_3H_7COOC_5H_{11}$	0·5982	94·5	10·8
$C_2H_5COOC_4H_9$	0·5621	73·0		$C_4H_9COOC_6H_{11}$	0·6123	105·3	

AROMATIC HYDROCARBONS.

Sp. heat at boiling-point calculated from $C = A + bt$.

Substance	Specific heat	Mol. heat	Diff.	Substance	Specific heat	Mol. heat	Diff.
C_6H_6	0·4672	36·4	9·4	$C_6H_5C_2H_5$ . .	0·5347	56·8	11·0
$C_6H_5CH_3$ . .	0·4984	45·8	11·0	$C_6H_5C_3H_7$ . .	0·5653	67·8	8·6
$C_6H_5C_2H_5$ . .	0·5347	56·8		$C_6H_3(CH_3)_3$ $^{(1.2.4)}$	0·5702	76·4	

FATTY ACIDS.

Specific heat at boiling-point.

Substance	Specific heat	Mol. heat	Diff.	Substance	Specific heat	Mol. heat	Diff.
$HCOOH$ . . .	0·5675	26·1	10·6	C_2H_5COOH .	0·6424	47·4	12·0
CH_3COOH . .	0·6113	36·7	10·7	C_3H_7COOH .	0·6751	59·4	12·7
C_2H_5COOH .	0·6424	47·4		C_4H_9COOH .	0·7077	72·1	

ALLYL ESTERS.

Specific heat at boiling-point.

Substance	Specific heat	Mol. heat	Diff.	Substance	Specific heat	Mol. heat	Diff.
$CH_3COOC_3H_5$.	0·5220	52·2	9·5	$n. C_3H_7COOC_3H_5$	0·5588	71·5	9·8
$C_2H_5COOC_3H_5$	0·5412	61·7		$n. C_4H_9COOC_3H_5$	0·5694	80·8	9·3

the same at any given temperature (Table XIV.). It follows, therefore, that homologous esters must show a fairly constant difference in molecular heat whether the comparison is made at a uniform temperature, at their boiling-points, or at an equal fraction of their absolute temperatures.[1] Schiff, as already mentioned, calculated the specific heats of these compounds at the same fraction (0·6) of their critical temperatures. He also calculated the densities at the same temperature, and showed that the product of specific heat and density is constant. Stating this result in general terms, we may say that equal volumes of the esters at equal fractions of their absolute critical temperatures have the same heat capacity.

TABLE XVIII.

UNSATURATION.

Specific heat measured at 20–100° C.[2]

Substance.	Sp. heat.	Mol. heat.	Differ. for H_2.
Diallyl	0·4975	40·8	2 × 5·4
Hexane.	0·6000	51·6	
Allyl alcohol	0·6441	37·4	3·3
Propyl alcohol . . .	0·6786	40·7	
Allyl acetate	0·4791	47·9	1·8
Propyl acetate . . .	0·4880	49·7	
Benzene	0·433	33·8	2 × 3·5
Diallyl	0·4975	40·8	

Specific heat calculated [3] at 0° C.

Propyl valerianate . .	0·4416	63·6	2·1
Allyl valerianate . .	0·4330	61·5	
Allyl benzoate . . .	0·3732	60·5	3·8
Propyl benzoate . . .	0·3830	64·3	
Allyl succinate . . .	0·4323	85·5	1·5 × 2
Propyl succinate . . .	0·4391	88·6	
Allyl chloracetate . .	0·3888	52·3	3·2
Propyl chloracetate . .	0·4067	55·5	

[1] The boiling-points and critical temperatures of homologous series are additive properties.

[2] Von Reis, *Wied. Ann.*, 13, 447 (1881).

[3] Calculated from Schiff's data with the aid of $C_t = A + 2bt$.

Unsaturation and Substitution.—Von Reis, Schiff, and Mabery and Goldstein have studied the effect of unsaturation. As a general rule, an unsaturated compound has a lower specific and molecular heat than the saturated substance which differs from it by H_2. A few of the results are given to show that the effect of loss of H_2 varies considerably according to the constitution of the body. The constitutive nature of molecular heat is here apparent.

The replacement of hydrogen by chlorine leads to a rise in molecular heat, which is fairly constant in the eight comparisons made in the following list:—

TABLE XIX.

REPLACEMENT OF II BY Cl.

Specific heat calculated [1] at o° C.

Substance.	Sp. heat.	Mol. heat.	Difference.
$CH_2ClCOOCH_3$ . .	0·3747	40·6	2·7
$CHCl_2COOCH_3$ . .	0·3032	43·3	2·7
CCl_3COOCH_3 . .	0·2592	46·0	
$CH_2ClCOOC_2H_7$ . .	0·4067	55·5	2·5
$CHCl_2COOC_2H_7$ . .	0·3335	57·0	2·4
$CCl_3COOC_2H_7$ . .	0·2892	59·4	
$CH_2ClCOOC_2H_5$ . .	0·390	47·7	2·7
$CHCl_2COOC_2H_5$ . .	0·3215	50·4	2·7
$CCl_3COOC_2H_4$ . .	0·2778	53·1	
$CH_2ClCOOC_2H_5$ . .	0·3888	52·2	2·6
$CHCl_2COOC_2H_5$ . .	0·3244	54·8	2·3
$CCl_3COOC_3H_4$ . .	0·2806	37·1	

The replacement of hydrogen by oxygen also causes a rise in molecular heat.[2]

§ 6. *MIXTURES OF NON-ELECTROLYTES*

We have seen that the specific heat of simple compounds is approximately equal to the sum of the atomic heats of the constituent atoms, and therefore it is to be expected that mixtures should show the same relations. Thus, assuming that the specific heats of the constituents of a mixture are the same as when unmixed, we may equate the heat capacities

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[1] Calculated from Schiff's data with the aid of $C_t = A + 2bt$.

[2] Von Reis, *Wied. Ann.*, **13**, 447 (1881).

of the mixture with the sum of the heat capacities of the constituents

$$C.P. = c_1 p_1 + c_2 p_2 + \text{etc.}$$

where C and P are the specific heat and mass of the mixture, and c_1, c_2, etc., p_1, p_2, etc., are the specific heats and masses of the unmixed constituents. Since

$$P = p_1 + p_2 + \text{etc.}$$

we may write

$$C = \frac{c_1 p_1 + c_2 p_2 + \text{etc.}}{(p_1 + p_2 + \text{etc.})}$$

With most liquid mixtures this expression for the specific heat holds good, but there are cases which do not conform to it. In all these the discrepancy can be accounted for by the state of association of the liquid, or by the formation of some unstable complex which breaks down on being heated.

(a) *Alloys.*—Alloys obey this admixture rule at temperatures sufficiently below their melting-point; at temperatures near the point of fusion the specific heat is always greater than that calculated. Regnault[1] first observed this with alloys of bismuth, tin and lead. His results were subsequently confirmed by Schuz.[2]

TABLE XX.

Alloy.		Melting-point.	Specific heat.		Calculated from formula.
			89–15°.	+15 to –77°.	
48·9 Bi 27·54 Pb 23·56 Sn	} Rose's alloy . .	90°	0·055	0·0355	0·0355
49·25 Bi 21·21 Sn 27·55 Pb	} d'Arcet's alloy .	95°	0·058	0·0348	0·0344
62·7 Hg 37·3 Sn	} HgSn . . .	135°	0·735	(–25 to +15°) 0·0432	0·0412
54·3 Sn 45·7 Hg	} HgSn$_2$ . . .	170°	0·0652	(–25 to +15°) 0·0460	0·0471

[1] *Ann. Chim. Phys.*, [3] 1, 129 (1841); *Pogg. Ann.*, 53, 60, 243 (1841).
[2] *Wied. Ann.*, 46, 177 (1892).

Spring[1] compared the amount of heat taken up by an alloy of tin and lead, when warmed from 100° to 360°, with the sum of the quantities absorbed by the constituents when heated separately through the same interval. It was found that the alloy had always the greater heat capacity, but the excess varied with the composition. Some of the results are quoted in the following table.

TABLE XXI.

HEAT ABSORBED BY 100 GRAMS OF—

Constituents.	Composition.	Alloy.	Difference.
Pb_4Sn . .	1735·9	2006·1	270·2
Pb_3Sn . .	1793·7	2176·3	382·6
Pb_2Sn . .	1895·1	2323·0	427·9
PbSn . . .	2129·8	2530·0	400·2
$PbSn_2$ . .	2410·1	2854·2	444·1
$PbSn_3$ . .	2572·3	3092·0	519·7
$PbSn_4$ . .	2678·3	3285·0	606·7
$PbSn_5$ . .	2752·1	3440·0	687·9
$PbSn_6$ . .	2808·2	3318·7	510·5

Regnault's determinations are added to show that at lower temperatures the specific heat of the alloy agrees with that calculated from the admixture rule.

	Spec. heat calculated.	Observed.
PbSn	0·0407	0·0404
$PbSn_2$	0·0450	0·0446

All these results may be explained by assuming that the metals form unstable compounds, which, on being heated, break down into their constituents. It has been shown in a former paragraph that under these conditions the intermolecular work, and consequently the specific heat, must be greater than when the decomposition does not take place.

(*b*) *Mixtures of Organic Compounds.*—Bussy and Buignet[2]

[1] *Bull. Acad. Belg.*, [3] 11, 355 (1886).
[2] *Ann. Chim. Phys.*, [4] 4, 5 (1865).

·first showed that with many liquid mixtures the observed specific heat is greater than the average value obtained by calculation from the specific heats of the components. Their observations were confirmed by Schuller,[1] who pointed out that mixtures containing alcohol always exhibited this abnormal behaviour. Liquid mixtures may be divided into three classes—

1. Normal mixtures. In these cases the observed specific heat agrees with that calculated from the admixture formula :

$$C = \frac{c_1 p_1 + c_2 p_2}{p_1 + p_2}$$

The chief mixtures of this type which have been investigated are—

Chloroform and carbon disulphide.[2, 3]
Benzene and carbon disulphide.[2, 3, 4]
Chloroform and benzene.[2, 3]
Heptane and chloroform.[3]
Heptane and carbon disulphide.[3]
Heptane and ethyl acetate.[3]

2. Mixtures whose specific heats are smaller than those of either constituent.

Benzene and aniline,[3]
Benzene and ethyl acetate,[3]
Benzene and acetic acid,[3]

may be quoted as typical cases.

3. Mixtures whose specific heats are greater than those of either component,[5] such as—

[1] *Pogg. Ann.*, **144**, *Ergänsungsband*, **5**, 116, 192 (1871).
[2] Schuller, *Pogg. Ann. Ergänzungsband*, **5**, 116, 192 (1871).
[3] Timofejew, *Chem. Centralblatt*, **2**, 429 (1905).
[4] Winkelmann, *Pogg. Ann.*, **150**, 592 (1873).
[5] For other mixtures of each type the reader should refer to Timofejew (*loc. cit.*).

Methyl alcohol and water.[2, 4, 5, 6, 7, 9, 13]

Ethyl alcohol and water.[1, 2, 3, 7, 8, 9, 11, 12, 13]

Propyl alcohol and water.[2, 5, 7, 9, 13]

Acetic acid and water.[10, 13]

Ethyl alcohol and benzene,[1] chloroform,[1] or carbon bi-sulphide.[1]

Glycerine and alcohol.[12]

Inspection of these lists will show that the normal mixtures contain liquids which are either weakly or non-associated. It may be assumed that on mixing them no change in molecular complexity takes place ; hence the specific heat of the mixture is equal to the average of the specific heats of the components. To explain the behaviour of those of the second class it must be assumed that when mixed the constituents suffer a diminution in molecular complexity. The heat spent on intra-molecular work will then be less than with the unmixed liquids, and accordingly the specific heat will be smaller. The third class contains liquids such as the alcohols, which are known not only to be associated, but also to be especially inclined to form molecular compounds. Accordingly, we find that the observed specific heats of these mixtures are larger than the calculated values. The divergence from the normal is relatively large, and varies in magnitude according to the composition of the liquid. To illustrate this, the following data are taken from the observations of Bose. The right-hand column shows the difference between the experimental and calculated specific heats.

[1] Schuller, *Pogg. Ann. Ergänzungsband*, **5**, 116, 192 (1871).

[2] Timofejew, *Chem. Centralblatt*, **2**, 429 (1905).

[3] Winkelmann, *Pogg. Ann.*, **150**, 592 (1873).

[4] Lecher, *Wien. Ber.*, **76**, 2, 937 (1877).

[5] Pagliani, *Nuovo Cimento*, [3] **12**, 229 (1882).

[6] Dupré, *Proc. Roy. Soc.*, **20**, 336 (1872).

[7] Zettermann, *Journal de Physique*, **10**, 312 (1881).

[8] Dupré and Page, *Phil. Mag.*, [4] **38**, 158 (1869).

[9] Bose, *Zeit. Phys. Chem.*, **58**, 585 (1906).

[10] Von Reis, *Wied. Ann.*, **10**, 291 (1880).

[11] Jamin and Amaury, *Comptes Rend.*, **70**, 1237 (1870).

[12] *Physical Review*, **9**, 65 (1899).

[13] Muller and Fuchs, *Comptes Rendus*, **140**, 1639 (1905).

TABLE XXII.

Specific Heats of Mixtures of Methyl Alcohol and Water.

Percentage of alcohol.	Specific heat, at 0·5–5·1° C.	Specific heat. Calculated from admixture formula.	Difference : observed and calculated.
0	1·006	—	—
5	1·023	0·984	0·039
10	1·019	0·962	0·057
15	0·999	0·941	0·058
20	0·973	0·919	0·054
25	0·947	0·897	0·050
30	0·921	0·875	0·046
35	0·894	0·853	0·041
40	0·869	0·832	0·037
45	0·844	0·810	0·034
50	0·818	0·788	0·030
55	0·793	0·766	0·027
60	0·768	0·744	0·024
65	0·744	0·723	0·021
70	0·720	0·701	0·019
75	0·696	0·679	0·017
80	0·673	0·657	0·016
85	0·649	0·635	0·014
90	0·625	0·614	0·011
95	0·600	0·592	0·008
100	0·570	—	—

Ethyl Alcohol and Water.

	at 0·5–5·0° C.		
0	1·005	—	—
5	1·026	0·982	0·044
10	1·042	0·958	0·084
15	1·045	0·936	0·109
20	1·037	0·913	0·124
25	1·019	0·890	0·129
30	0·998	0·867	0·131
35	0·971	0·844	0·127
40	0·934	0·821	0·113
45	0·896	0·798	0·098
50	0·863	0·774	0·089
55	0·832	0·751	0·081
60	0·802	0·728	0·074
65	0·772	0·705	0·067
70	0·741	0·682	0·059
75	0·710	0·659	0·051
80	0·679	0·636	0·043
85	0·648	0·613	0·035
90	0·615	0·590	0·025
95	0·582	0·567	0·015
100	0·544	—	—

According to the above views the magnitude of the difference between the experimental and calculated specific heats will be a measure of the heat expended in breaking up molecular complexes. Hence, in a series of mixtures of two substances, the one which exhibits the maximum divergence will probably be at the maximum stage of association. If in the case of methyl alcohol and water the divergence is plotted out against the percentage of alcohol in the mixture, the maximum is found very close to fifteen per cent. The liquid then has the composition $CH_3OH . 11 H_2O$.

With ethyl alcohol the maximum occurs at $C_2H_5OH . 6H_2O$. Acetic acid and water exhibit two maximum points, one of which corresponds to $CH_3COOH . H_2O$. Other physical properties of these solutions correspond with the specific heat. Dupré and Page[1] and Bose[2] have shown that the heat evolved on mixing an alcohol with water attains the maximum in the mixture of greatest specific heat. Moreover Jamin and Amaury[3] claim that the maxima of specific heat and density coincide, but this seems not to be[4] a general rule.

Marignac's[5] determinations of the specific heats of solutions of bromine, iodine, sulphur, and phosphorus in carbon disulphide show that these mixtures are normal. The case of sulphur is the most interesting. The data show that whilst concentrated solutions are normal, dilute solutions are abnormal, the specific heat of sulphur decreasing with advancing dilution. If n grammolecules of CS_2 contain one atom of sulphur, then $S + nCS_2$ may be called the molecular weight of the solution. If this be written as P, then the molecular heat of the solution

$$PC = Sc' + n . CS_2c''$$

where $c' =$ specific heat of sulphur, and c'' is that of carbon disulphide. The value of c'' is assumed to be the same as for

[1] *Pogg. Ann. Ergänzungsband*, **5**, 221 (1871); and *Proc. Roy. Soc.*, **20**, 336 (1872).

[2] *Zeit. Phys. Chem.*, **58**, 592 (1906).

[3] *Compt. Rend.*, **70**, 1237 (1870).

[4] Wüllner, *Pogg. Ann.*, **140**, 478 (1870); Pagliani, *Nuovo Cimento*, [3] **12**, 229 (1882).

[5] *Ann. Chim. Phys.*, [4] **22**, 385 (1871).

the pure solvent, so that CS_2c'', the molecular heat of the carbon disulphide in the solution, is equal to 18·1.   The atomic heat of sulphur is then—

$$Sc' = PC - 18·1n$$

The values for this expression obtained by Marignac at varying dilutions are given below.

SPECIFIC HEAT OF SULPHUR DISSOLVED
IN CS_2.

n	PC.	PC — 18·1n.
1	24·7	6·6
2	42·8	6·6
4	77·9	5·5
10	186·0	5·0

The latter values for the atomic heat of sulphur agree fairly well with those found for the solid element.

Magie, in a theoretical discussion[1] of the specific heat of solutions, claims that the varying character of these is due to their different behaviour with respect to osmotic pressure.   He further shows that if the osmotic pressure of the dissolved substance is proportional to the absolute temperature, the solution will behave normally and obey the admixture rule.   Solutions of electrolytes and those in which combination between solvent and solute takes place must be abnormal.   Magie's experimental work is also of great interest.   He determined the molecular heat of several organic solids in aqueous and other solutions.   Many of the aqueous solutions examined were normal, the solute and solvent preserving the same molecular heat at all dilutions.   The molecular heat of the dissolved substance was calculated in a manner similar to that employed by Marignac and others.   It is assumed that the specific heat

[1] *Physical Review,* **9**, 65 (1899); **13**, 91 (1901); **16**, 381 (1903); **17**, 105 (1903).   See also Tammann, *Zeit. Phys. Chem.,* **18**, 625 (1885), and Püschl, *Wien. Ber.,* **109**, 981 (1901); and *Monatshefte für Chemie,* **22**, 77 (1901).

of the solvent is unaltered by the presence of the solute ; then, remembering that

$$Mc' = PC - 18n$$

where P = average molecular weight of the solution,

　　C = specific heat of the solution found by experiment,

　　n = number of gram-molecules of solvent to one of solute,

　　18 = molecular heat of water,

M and *c'* = molecular weight and specific heat of solute,

it is possible to calculate the apparent molecular heat (M*c'*) of the dissolved substance.

The example of cane sugar in aqueous solution is given below ; and it will be seen that the molecular heat is constant at all dilutions.

CANE SUGAR IN WATER.

n.	C.	M*c'*.
50	0·8479	153·1
100	0·9115	152·5
150	0·9375	150·0
250	0·9609	152·7

Average molecular heat of cane sugar = 152·6.

The molecular heats of glycerine in ethyl alcohol and of ethyl alcohol in water varied with the concentration; these solutions are abnormal.   The general results of the investigation were that—

(1) The molecular heat of a substance differs in the solid and dissolved states.

(2) The molecular heat of a body differs in different solvents.

(3) That isomeric substances may have different molecular heats.

The last-named conclusion serves to demonstrate the constitutive nature of molecular heat.   Some illustrations of these results are collected in the appended table.

TABLE XXIII.

MOLECULAR HEATS OF SOLIDS.

Substance.	Free.	In aqueous solution.
Cane sugar	103	152·6
Maltose	116	143·0
Dextrose.	56·5	78·8
Mannite	57·5	108·0
Urea	19·2	21·5
Resorcinol	29·2	63·5

MOLECULAR HEATS IN DIFFERENT SOLVENTS.

Substance.	Water.	Alcohol.
Resorcinol	63·5	56·7
Hydroquinone . . .	63·4	56·7

MOLECULAR HEATS OF ISOMERS IN AQUEOUS SOLUTION.

Levulose . .	56·5	Dulcite. . .	97·5
Dextrose .	89·6	Mannite . .	108·0
Maltose . .	142·7	Pyrocatechol .	63·5
Milk sugar . .	144·5	Resorcinol . .	75·5

It should be noted that the effect of temperature on the specific heat of aqueous solutions is only very slight.[1]

§ 7. *AQUEOUS SOLUTIONS OF ELECTROLYTES*

It cannot be said that the results obtained from the specific heats of aqueous solutions of electrolytes are commensurate with the amount of labour expended on their investigation. The earliest investigations—those of Schüller, Thomsen, and Marignac—contain the most important data. Schüller's[2] results showed that the specific heat of a salt solution is less than that

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[1] Magie, *Physical Review*, 9, 65, 1899; also for the effect of temperature on solutions of electrolytes, see Teudt, *Beiblätter*, 24, 1104 (1900); and Marignac, *Ann. Chim. Phys.*, [5] 8, 410 (1876).

[2] *Pogg. Ann.*, 136, 70 (1869).

calculated by the admixture rule. If the specific heat of the solid salt is represented by k, and if the solution contains p grams of salt to 100 grams of water, then the admixture rule demands that

$$c = \frac{100 + pk}{100 + p}$$

Schüller formulated his results as—

$$c = \frac{100 + pk}{100 + p} \cdot r$$

where r is constant, and in the cases examined less than unity. This method of expressing the specific heat of a salt solution is inaccurate, for, as Thomsen pointed out, when the proportion of salt diminishes, r must approach unity, and hence for very dilute solutions r cannot remain constant. Thomsen's [1] experiments were more extensive. He not only showed that the specific heat of a salt solution is usually less than that calculated, but was also able to trace the influence of dilution. Thomsen calculated at different dilutions the values [2] of PC, the molecular heat of the solution; and of PC $- n \times 18$, the molecular heat of the dissolved salt. PC may also be called the water value of the solution. Three typical cases are quoted in the subjoined table. It will be seen that the value of PC $- 18n$—the apparent molecular heat of the salt—diminishes as the dilution is increased; in the stronger solution it sometimes has a positive value, but in the more dilute the value is always negative. The numbers given under the heading PC express the water values of the solution; that is, the weight of water which requires the same amount of heat as the molecular weight of the solutions. In dilute solutions the water value falls below the molecular heat of the water present.

Marignac's elaborate experiments [3] lead to the same con-

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[1] *Zeitschrift für Chemie*, 1870, p. 729; *Pogg. Ann.*, **142**, 337 (1871); Winkelmann, *Pogg. Ann.*, **140**, 1 (1873), has contrasted Schüller's and Thomsen's data with those obtained by calculation from the heats of solution at different temperatures.

[2] See p. 178.

[3] *Ann. Chim. Phys.*, [4] **22**, 385 (1871); [5] **8**, 410 (1876).

TABLE XXIV.

SPECIFIC HEAT OF SODIUM CHLORIDE + nH$_2$O.

n = number of molecules of water present to one of solute.

n	Specific heat.	Molecular weight of solution.	Molecular heat PC.	PC − 18n
10	0·791	58·5 + 180	188·5	+ 8·5
20	0·863	58·5 + 360	361·0	+ 1·0
30	0·895	58·5 + 540	536·0	− 4
50	0·931	58·5 + 900	892·0	− 8
100	0·962	58·5 + 1800	1788	− 12
200	0·978	58·5 + 3600	3578	− 22

POTASSIUM HYDRATE + nH$_2$O.

30	0·876	56 + 540	522	− 18
50	0·916	56 + 900	876	− 24
100	0·954	56 + 1800	1770	− 30
200	0·975	56 + 3600	3565	− 35

SODIUM NITRATE + nH$_2$O.

10	0·769	85 + 180	203·8	+ 23·8
25	0·863	85 + 450	461·7	+ 11·7
50	0·918	85 + 900	904·0	+ 4
100	0·950	85 + 1800	1791	− 9
200	0·975	85 + 3600	3593	− 7

clusions. He also attacked the question whether a given replacement in a salt of either the acid or base by an equivalent of another always causes the same difference in molecular heat. With a few replacements he found an approximately constant value, and in the salts which behave thus, we may say that the molecular heat in dilute solution is approximately equal to the sum of two factors, those of the base and acid. This cannot, however, be stated as a general rule, for the exceptions are almost as numerous as the coincidences. It is important to notice that both Thomsen and Marignac found that certain salts give larger values for their specific heats than the admixture formula demands. In these the value of PC − 18n is always positive. Acetates and salts of other organic acids behave in this manner.

Two formulae have been proposed to express the specific

heat of a dilute salt solution. That of Matthias [1] expresses a relation between the specific heat and concentration of the solution, thus—

$$C = \frac{a + n}{b + n} \cdot c$$

where C = specific heat of the solution,

    c = specific heat of the solvent,

    n = number of solvent molecules present to one of solute ;

    a and *b* are constants.

The specific heat of a salt solution calculated by this formula agrees very well with that found experimentally ; but in this respect Magie's formula is somewhat better ; moreover it can be deduced from theory. Both Tammann [2] and Magie [3] have pointed out that the work of Thomsen and Marignac shows that in saline solutions the presence of the salt diminishes the total heat capacity of the water present. This is evident from the fact that the water value of the solution falls below the value of the total water present. Now, this can be accounted for by supposing that each molecule of undissociated salt and each ion collects a group of water molecules around itself. Further, the molecules of water which enter these loose complexes may have a different heat capacity from those remaining outside in the bulk of the solvent. The heat capacity of a salt solution will then be equal to the sum of the heat capacities of—

1. The water outside the complexes.

2. The groups composed of an undissociated molecule and its water shell.

3. The ions and their water shells.

If, then, we write—

[1] *Comptes Rend.*, **107**, 524 (1888) ; *Journ. de Phys.*, **8**, 204 (1889) ; also Cattaneo, *Nuovo Cimento*, [3] **26**, 50 (1889).

[2] *Zeit. Phys. Chem.*, **18**, 625 (1885).

[3] *Bulletin of Amer. Phys. Soc.*, April 27, 1901 ; *Physical Review*, **25**, 17 (1907).

M, S, N, as the molecular weight, specific heat, and total number of molecules of water present;

m, n, as the molecular weight and number of molecules of solute;

a, α, as the number of water molecules affected by one undissociated gram-molecule of solute, and the number affected by one dissociated gram-molecule;

s, σ, as the specific heats of the groups containing undissociated and dissociated molecules of solvent; and

p as the number of gram molecules dissociated;

we may equate the total heat capacity of the solution with the sum of the heat capacities of the component parts; thus—

$$H = S[MN - a(n - p)M - \alpha p M]$$
$$+ s(m + aM)(n - p)$$
$$+ \sigma(m + \alpha M)p$$

Hence—

$$H =$$
$$SMN + (sm + saM - SaM)(n - p) + (\sigma m + \sigma\alpha M - S\alpha M)p$$

Then, writing the expressions $(sm + saM - SaM)$ and $(\sigma m + \sigma\alpha M - S\alpha M)$ as A and B respectively, we have—

$$H = SMN + A(n - p) + Bp$$

In this expression it will be noticed that SMN is the total heat capacity of the water as if it were separate; and further, that A and B respectively depend on the undissociated molecules and on the ions and the manner in which they affect their adherent water molecules. With non-electrolytes or with electrolytes in the undissociated state we have—

$$H = SMN + An$$

and at complete dissociation

$$H = SMN + Bn$$

If, now, in a solution there are N molecules of water

present to one of solute, p becomes the ionisation factor and—

$$H = SMN + A - Ap + Bp$$

This, after inserting

$$A + C = B$$

becomes

$$H = SNM + A + Cp$$

The latter expression gives an accurate measure of the molecular heat of a salt solution. To show the agreement between theory and practice the following cases are given in detail.

<div align="center">

TABLE XXV.

SODIUM CHLORIDE.

$A = 39.$ $C = -70.$

</div>

N.	$NaCl + N.H_2O$.	p.	Molecular heat (observed).	Molecular heat (calculated).
10	$58·5 + 180$	0·42	188·5 (Thomsen)	189·6
20	$58·5 + 360$	0·544	361	361
30	$58·5 + 540$	0·613	536	536·1
50	$58·5 + 900$	0·668	892	892·2
100	$58·5 + 1800$	0·729	1788	1788
200	$58·5 + 3600$	0·780	3578	3584·4

<div align="center">

SODIUM HYDROXIDE.

$A = 32.$ $C = -65·6.$

</div>

N.	$NaOH + N.H_2O$.	p.	H (obs.).	H (calc.).
30	$40 + 540$	0·602	533	533
50	$40 + 900$	0·696	815	886
100	$40 + 1800$	0·775	1711	1781
200	$40 + 3600$	0·824	3578	3578

The constant B in the original equation represents the heat capacity of a gram-molecule of a dissociated salt and the water associated with it, less the heat capacity of the water when not associated with the ions. Some values for B as obtained

from $A + C = B$ are given in the following list. It will be seen that the replacement of one ion by another causes an approximately constant difference in the value.

Replacement of Na by K.			Replacement of Cl by NO₃.		
Salt.	B.	Diff.	Salt.	B.	Diff.
NaCl . . .⎱	-31 ⎱	22	KCl . . .⎱	-53 ⎱	11
KCl . . .⎰	-53 ⎰		KNO₃ . .⎰	-42 ⎰	
NaOH . .⎱	$-33 \cdot 6$ ⎱	17·4	NaCl . .⎱	-31 ⎱	11
KOH . .⎰	-51 ⎰		NaNO₃ .⎰	-20 ⎰	
NaNO₃ . .⎱	-20 ⎱	22	½BaCl₂ . .⎱	-55 ⎱	10
KNO₃ . .⎰	-42 ⎰		½Ba(NO₃)₂ ⎰	-45 ⎰	

If it be assumed that an ion has the same heat capacity as the atom or group in a solid, then by subtracting this value for each ion from B, we can obtain the amount by which the heat capacity of the water associated with the ions is diminished. The justice of the assumption is evident from the fact that a nearly constant value for the difference is obtained. It is, however, remarkable that the salts fall into two groups.

TABLE XXVI.

Salt.	B.	h.	B − h.	Salt.	B.	h.	B − h.
NaCl . .	-31	12·5	$-43 \cdot 5$	KCl . .	-53	12·8	$-65 \cdot 8$
NH₄Cl . .	$-23 \cdot 1$	20·9	-44	KNO₃ . .	-42	24·1	$-66 \cdot 1$
NaNO₃ . .	-20	23·6	$-43 \cdot 6$	KOH . .	-51	13·3	$-64 \cdot 3$
NaOH . .	$-33 \cdot 6$	13·3	$-46 \cdot 9$	½BaCl₂ . .	-55	9·4	$-64 \cdot 4$
HCl . . .	-37	8·8	$-45 \cdot 8$	½SrCl₂ . .	$-59 \cdot 4$	9·5	$-68 \cdot 9$
				½Ba(NO₃)₂	-45	19·9	$-64 \cdot 9$

From the values of $B - h$ Magie shows that it is possible to form an estimate of the minimum number of molecules of water attached to each ion.

If all ions affect the specific heat of their water shells to an equal degree, it is clear that different ions are enclosed by shells of different sizes. In this connection the reader is

referred to the work of Carroll on the viscosity of electrolytes.[1]

Kalikinsky[2] also has studied the connection between ionisation and specific heat. He finds that at great dilution equivalent quantities of electrolytes lower the specific heat of the solvent by an equal amount; and further, that the specific heat decreases with increasing conductivity. From Magie's work the former conclusion would seem not to be generally true.

§ 8. *APPLICATIONS OF SPECIFIC HEAT*

The chief direction in which specific heat has been applied is in the determination of atomic weights. Regnault, employing the atomic weights which were current at the time, found that the atomic heats of most elements were about 3. There were, however, three exceptions: sodium, potassium, and silver, whose atomic heats were nearly 6. He therefore desired to halve the atomic weights of these metals to bring them into accordance with the majority. This proposal for many reasons could not be accepted by chemists. Cannizzaro instead wished to invert Regnault's proposal by doubling the atomic weight of the elements which gave the lower atomic heat. The idea was at first met by many objections ; but they were gradually overcome, and the suggestion was adopted. It then became recognized that the atomic heat of an element is approximately 6. This fact has been often used to decide the atomic weight of a metal when the chemical evidence was indecisive.

Thallium shows considerable analogy with lead ; hence its salts might be thought to have an analogous composition. The chloride would then be $TlCl_2$; and since the equivalent of the metal is about 203, its atomic weight would be 406. On the other hand, thallium exhibits a close resemblance to the alkali metals, and accordingly the chloride would be $TlCl$ and

[1] Page 90.
[2] *Journ. Russ. Phys. Chem. Soc.*, **35**, 1215 (1904); and *Chem. Central-blatt.* I., 1121 (1904).

the atomic weight 203. Schmitz'[1] determination of the specific heat as 0·0300 decides in favour of the latter the quotient 6·3 ÷ 0·03 being 210.

Uranium, on account of its supposed resemblance to iron, was at first considered to have the atomic weight 120. Mendelejeff,[2] however, placed the element in the chromium group of the periodic table, and assigned to it the atomic weight 240. The earlier determinations of specific heat were indecisive ; but finally Zimmermann[3] obtained the value 0·027, and thus proved the correctness of Mendelejeff's suggestion. Indium has the equivalent 37·8. In certain respects this metal resembles zinc and cadmiun ; its salts were therefore given the formula $In''R_2$, whence the atomic weight would be 75·6. Bunsen[4] found the specific heat to be 0·057, and consequently the atomic weight was altered to 113·4. The atomic weights of cerium, lanthanum, and didymium were also decided in this way. The old atomic weights were Ce = 92, Di = 95, and La = 92. Mendelejeff,[5] considering the position which they should occupy in the periodic system, wished to alter these to Ce = 138, Di = 138, and La = 180. On the other hand, Rammelsberg[6] objected to this change on account of the crystallographic relations of these salts, which are isomorphous with those of yttrium and cadmium. Hillebrand's[7] determination of the specific heats of these elements decided the question. The values found were—

$$Ce = 0·04479, \ Di = 0·04563, \ La = 0·04485$$

whence the atomic weights should be one and a half times as great as those generally in use, viz.—

$$Ce = 138, \ Di = 144·8, \ and \ La = 139$$

[1] *Proc. Roy. Soc.*, **77**, 177 (1903) ; see also Regnault, *Ann. de Chim.*, [3] **67**, 427 (1863), who found 0·033.
[2] *Ann. Supplement*, **8**, 178 (1872).
[3] *Ber.*, **15**, 847 (1882).
[4] *Pogg. Ann.*, **141**, 1 (1870).
[5] *Ann. Suppl.*, **8**, 186 (1872).
[6] *Ber.*, **6**, 84 (1873).
[7] *Pogg. Ann.*, **158**, 71 (1876).

Further than to questions of this nature specific heat has not been extensively applied. It might possibly be employed to demonstrate the existence of unstable compounds in mixtures of non-electrolytes, since the specific heat of mixtures containing such compounds is abnormal. Magie, as we have seen, has been able by means of this property to obtain distinct evidence of the hydration of ions.

CHAPTER VI

FUSIBILITY AND CHEMICAL CONSTITUTION

§ 1. *INTRODUCTION*

THE melting-point of a compound is a property which organic chemists rarely fail to determine, especially if it lies within the range of an ordinary mercury thermometer. The mass of data at our disposal is therefore enormous, and it might be expected that the relations between melting-point and constitution would be developed to a corresponding degree. The subject, however, does not seem to have attracted chemists, perhaps on account of its extreme simplicity, and the lack of applications which can be found. Most chemists, working in a particular field of research, observe certain regularities in the compounds they meet with ; but attention is not drawn to these regularities and the casual reader of the journals does not notice them.

With inorganic compounds, the data are not so numerous. Generally speaking, inorganic substances melt at relatively high temperatures, and it is only of recent years that methods for accurately determining such melting-points have been developed. The accuracy with which the melting-point of an organic compound is usually measured may not be very great, but it is sufficient to reveal the effects of chemical constitution.

§ 2. *INORGANIC SUBSTANCES*

Like many other properties of the elements, the melting-point is a periodic function of the atomic weight.[1] When the

[1] Carnelley, *Phil. Mag.*, [5] 8, 315 (1879) ; *Phil. Mag.*, [5] 18, 1 (1884).

elements are arranged according to the periodic system, it is seen that the melting-points in different families follow in order according to the atomic weight. In the alkali metals and first group of heavy metals the melting-point rises with increasing atomic weight.

TABLE I.

Element.	M.P. (abs.)	Element.	M.P. (abs.)
Lithium	459°	Magnesium . . .	905°
Sodium	370°	Zinc	693°
Potassium . . .	335°	Cadmium . . .	594°
Rubidium	311°	Mercury	234°
Caesium	299°		

With the non-metals, the reverse is found, the fusibility falling with increased atomic weight.

Element.	M.P. (abs.)	Element.	M.P. (abs.)	Element.	M.P. (abs.)	Element.	M.P. (abs.)
Nitrogen .	63°	Oxygen .	73°	Fluorine .	50°	Argon .	85°
Phosphorus .	317	Sulphur .	388	Chlorine .	171	Krypton .	104
Arsenic . .	631	Selenium	490	Bromine .	266	Xenon .	133
Antimony .	998	Tellurium	719	Iodine .	387		
Bismuth . .	542						

In the families which lie between these the relations are variable.

Carnelley has also found regularities with the halogen derivatives of various families.

ORGANIC COMPOUNDS

§ 3. *HOMOLOGOUS SERIES*

In commencing the study of the relations between constitution and melting-point we shall examine the additive nature of the property, and endeavour to ascertain whether the change

in melting-point corresponding to a given difference in com-
position is constant for all classes of compounds. For this
purpose the study of homologous series and replacements is
necessary.

The melting-points of the members in a homologous series,
taken as a whole, show a general inclination to vary con-
tinuously with increasing molecular weight, and in by far the
greater number of cases the tendency is to rise. But in most
cases the increase in temperature of fusion caused by successive
methylene groups is not regular ; and, generally speaking, the
influence of homology falls off as the higher members are
reached.

In a few series, the effect of the additional methylene
group seems to become constant· in the members of high
molecular weight, whilst in others it seems to die out
altogether. Sometimes it is found that the magnitude of the
homologous effect alternates with each successive member of
the series, and in such cases the alternative members form
separate series, showing regularities among themselves.
This alternating effect is the most remarkable property
exhibited by the melting-points of homologues, and, in want
of a better, it may serve as a basis of classification. Thus
homologous series may be divided into—

  1. Non-alternating series.
  2. Alternating series.

Non-alternating Series.—As illustration of this type, the
alcohols, ketones, and fatty acid amides may be chosen. On
examining the following tables, it will be noticed that with the
alcohols and ketones the fusibility decreases as the series are
ascended ; also, it will be evident that the effect of additional
methylene is much greater in the lower members than with
the higher ; in the simple ketones there is some irregularity,
possibly owing to faulty observation. In both series the effect
of CH_2 is inclined to become constant in the higher terms.

In the fatty amides, after passing over the first three or
four members which are quite irregular, it is clear that the
melting-point becomes fairly constant from C_6 onwards.
In this series the addition of CH_2 makes little or no difference

in fusibility; but it is difficult to decide whether the melting-point is really constant, since it must be remembered that the data have been obtained by different observers, who usually do not agree in the values for the same substance, and who rarely state whether the temperatures are "corrected" or not. This uncertainty applies, of course, to all melting-point data.

TABLE II.

Alcohols.[1]			Ketones.		
Substance.	M.P.	Diff. for CH_2.	Substance.	M.P.	Diff. for CH_2.
CH_3OH . . .	$-94°$	-18	$CH_3COC_6H_{13}$ . .	$-16°$	$+1$
CH_3CH_2OH .	$-112°$	-15	$CH_3COC_7H_{15}$ . .	$-15°$	$18·5$
$CH_3CH_2CH_2OH$.	$-127°$	$+5$	$CH_3COC_8H_{17}$ . .	$+3·5°$	$11·5$
$CH_3(CH_2)_2CH_2OH$	$-122°$		$CH_3COC_9H_{19}$ . .	$+15°$	6
$CH_3(CH_2)_3CH_2OH$	$-36·5°$	18	$CH_3COC_{10}H_{21}$ . .	$21°$	7
$CH_3(CH_2)_4CH_2OH$	$-17·9°$	13	$CH_3COC_{11}H_{23}$ . .	$28°$	$5·5$
$CH_3(CH_2)_5CH_2OH$	$-5°$	12	$CH_3COC_{12}H_{25}$ . .	$33·5°$	$5·5$
$CH_3(CH_2)_6CH_2OH$	$+7°$	12	$CH_3COC_{13}H_{27}$ . .	$39°$	4
$CH_3(CH_2)_7CH_2OH$	$19°$	6	$CH_3COC_{14}H_{29}$ . .	$43°$	5
$CH_3(CH_2)_{10}CH_2OH$	$25°$	$5·5$	$CH_3COC_{15}H_{31}$ . .	$48°$	$3·5$
$CH_3(CH_2)_{11}CH_2OH$	$30·5°$	$7·5$	$CH_3COC_{16}H_{33}$ . .	$51·5°$	4
$CH_3(CH_2)_{12}CH_2OH$	$38°$	7	$CH_3COC_{17}H_{35}$ . .	$55·5°$	
$CH_3(CH_2)_{13}CH_2OH$	$45°$	$4·5$			
$CH_3(CH_2)_{14}CH_2OH$	$49·5°$				

NORMAL FATTY ACID AMIDES.

Substance.	M.P.	Substance.	M.P.
$HCONH_2$	$-1°$	$C_{11}H_{23}CONH_2$ . .	$110°$
CH_3CONH_2 . . .	$82°$	$C_{12}H_{25}CONH_2$ . .	$98·5°$
$C_2H_5CONH_2$ . . .	$79°$	$C_{13}H_{27}CONH_2$ . .	$102°$
$C_3H_7CONH_2$ . . .	$115°$	$C_{14}H_{29}CONH_2$ . .	$108°$
$C_4H_9CONH_2$ . . .	$114-116°$	$C_{15}H_{31}CONH_2$ . .	$106-7°$
$C_5H_{11}CONH_2$ . . .	$100°$	$C_{16}H_{33}CONH_2$ . .	
$C_6H_{13}CONH_2$ . . .	$95°$	$C_{17}H_{35}CONH_2$ . .	$108-9°$
$C_7H_{15}CONH_2$ . . .	$97-8°$	$C_{18}H_{37}CONH_2$ . .	
$C_8H_{17}CONH_2$ . . .	$99°$	$C_{19}H_{39}CONH_2$ . .	$108°$
$C_9H_{19}CONH_2$ . . .	$108°$	$C_{21}H_{43}CONH_2$ . .	$111°$
$C_{10}H_{21}CONH_2$ . .	$103°$	$C_{25}H_{51}CONH_2$ . .	$109°$

[1] Blau, *Monatshefte für Chem.*, **26**, 89 (1905).   Carrera and Coppadero, *Gazz.*, I. 329 (1903).

TABLE III.

NORMAL PARAFFINS.

Substance.	M.P.	Difference for CH₂.	Difference between odd members.	Difference between even members.
CH₄ . . .	−184°			
C₂H₆ . . .	−172	12		
C₉H₂₀ . . .	−51			
C₁₀H₂₂ . . .	−32	19	25	20
C₁₁H₂₄ . . .	−26	6		
C₁₂H₂₆ . . .	−12	14	20	17·5
C₁₃H₂₈ . . .	−6	6		
C₁₄H₃₀ . . .	+5·5	11·5	16	12·5
C₁₅H₃₂ . . .	10	4·5		
C₁₆H₃₄ . . .	18	8	12·5	10
C₁₇H₃₆ . . .	22·5	4·5		
C₁₈H₃₈ . . .	28	5·5	9·5	8·7
C₁₉H₄₀ . . .	32	4		
C₂₀H₄₂ . . .	36·7	4·7	8·4	7·7
C₂₁H₄₄ . . .	40·4	3·7		
C₂₂H₄₆ . . .	44·4	4·0	7·3	6·7
C₂₃H₄₈ . . .	47·7	3·3		
C₂₄H₅₀ . . .	51·1	3·4		
C₃₁H₆₄ . . .	68·1			
C₃₂H₆₆ . . .	70·0	1·9		

GLYCOLS.[1]

Substance.	M.P.	Difference for CH₂.	Difference between even members.
(CH₂)₂(OH)₂	− 12°		
(CH₂)₃(OH)₂	− 55	− 43	
(CH₂)₄(OH)₂	+ 16	+ 71	+ 28
(CH₂)₆(OH)₂	41		+ 25
(CH₂)₈(OH)₂	63		+ 22
(CH₂)₉(OH)₂	43·5	− 20	+ 8·5
(CH₂)₁₀(OH)₂	71·5	+ 28	

DIAMINES.[2]

Substance.	M.P.	Difference for CH₂.	Difference between even members.
(CH₂)₂(NH₂)₂	+ 8·5°	—	
(CH₂)₃(NH₂)₂	liquid	—	19·5
(CH₂)₄(NH₂)₂	+ 27°	—	
(CH₂)₅(NH₂)₂	liquid	—	13
(CH₂)₆(NH₂)₂	40°	− 12	
(CH₂)₇(NH₂)₂	28°	+ 23	11
(CH₂)₈(NH₂)₂	51°	− 14	
(CH₂)₉(NH₂)₂	37°	+ 24	10
(CH₂)₁₀(NH₂)₂	61°		

[1] Henry, *Bull. Acad. Roy. Belg.*, 1142 (1904).
[2] Kauffer, *Chemiker. Ztg.*, **25**, 133 (1901)

TABLE III.—*continued.*

NORMAL FATTY ACIDS (DIBASIC).[1]

Acid.	M.P.	Difference for CH$_2$.	Difference between odd members.	Difference between even members.
Oxalic, C$_2$ . .	189°			
Malonic, C$_3$ . .	132	− 57		− 4
Succinic, C$_4$ . .	185	+ 53	− 35	
Glutaric, C$_5$ . .	97	− 88		− 37
Adipic, C$_6$ . .	148	+ 51	+ 8	
Pimelic, C$_7$ . .	105	− 43		− 8
Suberic, C$_8$ . .	140	+ 35	+ 1	
Azelaic, C$_9$ . .	106	− 34		− 7
Sebacic, C$_{10}$ . .	133	+ 27	+ 4	
Nonane, C$_{11}$ dicarboxylic }	110	− 23		− 6
Decane, C$_{12}$ dicarboxylic }	127	+ 17	+ 4	
Brassylic, C$_{13}$ . .	114	− 13		

NORMAL FATTY ACIDS (MONOBASIC).[2]

Acid	M.P.	Difference for CH$_2$.	Difference between odd members.	Difference between even members.
HCOOH . . .	+ 8·6	+ 8		
CH$_3$COOH . .	+ 16·7	− 38·7	− 30·6	
C$_2$H$_5$COOH . .	− 22	+ 14		− 24·5
C$_3$H$_7$COOH . .	− 7·9	− 50·5	− 36·5	
C$_4$H$_9$COOH . .	− 58·5	+ 66·5		+ 16
C$_5$H$_{11}$COOH .	+ 8	− 18·5	+ 48	
C$_6$H$_{13}$COOH .	− 10·5	+ 27		+ 8·5
C$_7$H$_{15}$COOH .	+ 16·5	− 4	+ 23	
C$_8$H$_{17}$COOH .	12·5	+ 19		+ 15
C$_9$H$_{19}$COOH .	31·4	− 3	+ 16	
C$_{10}$H$_{21}$COOH .	28·5	+ 15		+ 12
C$_{11}$H$_{23}$COOH .	43·5	− 3	+ 12	
C$_{12}$H$_{25}$COOH .	40·5	+ 13·3		+ 10·3
C$_{13}$H$_{27}$COOH .	53·8	− 2·8	+ 10·5	
C$_{14}$H$_{29}$COOH .	51	+ 11·6		+ 8·8
C$_{15}$H$_{31}$COOH .	62·6	− 2·6	+ 9	
C$_{16}$H$_{33}$COOH .	60	+ 9·3		+ 6·7
C$_{17}$H$_{35}$COOH .	69·3	− 2·8	+ 6·5	
C$_{18}$H$_{37}$COOH .	66·5			

We may now consider some examples of the alternating type of series.

Alternating Series.—The normal paraffins, mono and dibasic fatty acids, diamines, and glycols, may be taken as typical examples of alternating character.   See Table III., p. 195.

[1] Baeyer, *Ber.*, **10**, 1286 (1877).
[2] Baeyer, *Ber.*, **10**, 1287 (1877).

In the paraffin series the addition of CH_2 causes an increase which at first shows alternation and then higher in the series becomes constant; thus the increment in melting-point from nonane—decane—undecane—dodecane alternates from 19–6° to 14–6°, whilst later on, from C_{18} to C_{24}, the increase is about 4°. It will be noticed that this shows the method of classification employed above to be unsound, for if it so happened that only the higher paraffins were known they would certainly have been classed as non-alternating.

The paraffins, however, display the alternating effect only to a slight extent, and in this they are rather exceptional; in the other series quoted a very marked change is found on passing through the consecutive members. In the acids, glycols, and diamines it can be seen on passing from a member with an even number of carbon atoms to the next with an odd number that the melting-point is actually lowered; with the paraffins the effect was only slight, and was merely sufficient to lessen the usual increase due to CH_2. So far as can be inferred from the present data, it seems to be a general rule that the alternating factor always exerts depression on the compound with an odd number of carbon atoms and raises the melting-points of those with an even number. The odd and even members may be separated into two series, of which the successive members differ by $2CH_2$. In the monobasic acids the effect of $2CH_2$ in either series is to increase the melting-point, but this falls off as the higher members are reached. With the dibasic acids the members of the even series suffer a decrease in melting-point on the addition of $2CH_2$, whilst the contrary is found with the odd members.

Inspection of the lists will also show that the alternating effect becomes less and less as the series are ascended; thus in the paraffins it entirely disappears, but in the other series it is merely lessened.

§ 4. *REPLACEMENTS*

Franchimont[1] has collected data to display the influence of replacing hydrogen by various groups, but the study of

[1] *Rec. Pays Bas.*, **16**, 126 (1897). Numerous other replacements have

these replacements is not very profitable, and only a few need be mentioned. The entry of oxygen into a compound is almost universally accompanied by a rise in melting-point. This is illustrated by the accompanying lists.

TABLE IV.
REPLACEMENT OF H_2 BY $=O$.

Substance.	M.P.	M.P.	Substance.
$C_{11}H_{23}CH_3$	$-12°$	$44·5°$	$C_{11}H_{23}CHO$
$C_{13}H_{27}CH_3$	$+5·4$	$52·5$	$C_{13}H_{27}CHO$
$C_{15}H_{31}CH_3$	$18·2$	$58·5$	$C_{15}H_{31}CHO$
$C_{17}H_{35}CH_3$	$28·0$	$63·5$	$C_{17}H_{35}CHO$
$C_{11}H_{23}CH_2CH_3$ . .	$-6·2$	28	$C_{11}H_{23}COCH_3$
$C_{13}H_{27}CH_2CH_3$ . .	$+10$	39	$C_{13}H_{27}COCH_3$
$C_{15}H_{31}CH_2CH_3$ . .	$22·5$	48	$C_{15}H_{31}COCH_3$
$C_{17}H_{35}CH_2CH_3$ . .	32	$55·5$	$C_{17}H_{35}COCH_3$
$C_6H_5CH_2CH_2C_6H_5$.	52	60	$C_6H_5CH_2COC_6H_5$
$C_6H_5CH_2C_6H_5$ . . .	26	46	$C_6H_5COC_6H_5$
$C_6H_5CH_2CH_3$ . . .	liquid	20	$C_6H_5COCH_3$
$(C_5H_{11})_2CH_2$ . . .	$-26·5$	$14·6$	$(C_5H_{11})_2CO$
$(C_6H_{13})_2CH_2$ . . .	$-6·2$	30	$(C_6H_{13})_2CO$
$(C_7H_{15})_2CH_2$ . . .	$+10$	40	$(C_7H_{15})_2CO$
$(C_9H_{19})_2CH_2$ . . .	32	58	$(C_9H_{19})_2CO$
$(C_{11}H_{23})_2CH_2$ . .	$47·7$	69	$(C_{11}H_{23})_2CO$
$(C_{13}H_{27})_2CH_2$ . .	$59·5$	77	$(C_{13}H_{27})_2CO$
$(C_{15}H_{31})_2CH_2$ . .	$68·1$	83	$(C_{15}H_{31})_2CO$
$(C_{17}H_{35})_2CH_2$ . .	$74·7$	$88·4$	$(C_{17}H_{35})_2CO$

REPLACEMENT OF H BY OH.

$(C_6H_{13})_2CH_2$ . . .	$-6·7$	42	$(C_6H_{13})_2CHOH$
$(C_{11}H_{23})_2CH_2$ . .	$+47·7$	76	$(C_{11}H_{23})_2CHOH$
$(C_{15}H_{31})_2CH_2$ . .	$68·1$	85	$(C_{15}H_{31})_2CHOH$
$C_6H_5CH_2C_6H_5$ . .	26	68	$C_6H_5CHOHC_6H_5$
$C_6H_5COCH_2C_6H_5$.	60	134	$C_6H_5COCHOHC_6H_5$

ADDITION OF OXYGEN.

$(C_6H_5)_2S$	liquid	70	$(C_6H_5)_2SO$
$(CH_3OC_6H_4)_2S$ . .		115	$(C_6H_4OCH_3)_2SO$
$(C_6H_5)_2SO$ . . .	70	128	$(C_6H_5)_2SO_2$
$(C_6H_5)_3P$	75	143	$(C_6H_5)_3PO$
$C_6H_5N(CH_3)_2$ . . .	$0·5$	153	$(C_6H_5N(CH_3)_2O$
C_6H_5I	-30	210(decom.)	C_6H_5IO
$(CH_3CO)_2O$ . . .	liquid	30	$(CH_3CO)_2O_2$

been dealt with also by Marckwald, *Lehrbuch der Chemie*, Graham-Otto, vol. i. 3 (1897).

The reverse effect is usually found when a methyl group is introduced in place of hydrogen, which is attached to oxygen, nitrogen, or sulphur.

TABLE V.

Substance.	M.P.	M.P.	Substance.
C_6H_5OH	43°	liquid	$C_6H_5OCH_3$
$C_6H_4OH . CH_3(1·4)$.	36	liquid	$(1·4)C_6H_4OCH_3 . CH_3$
CH_3COOH . . .	16·7	− 101·2°	CH_3COOCH_3
$HCONH_2$	− 1	liquid	$HCONHCH_3$
CCl_3CONH_2 . . .	154	91	$CCl_3CONHCH_3$
$C_6H_5CONH_2$ . . .	128	78	$C_6H_5CONHCH_3$
$CO(NH_2)_2$	132	102	$NH_2CONHCH_3$
$C_6H_5CH_2CONH_2$.	155	58	$C_6H_5CH_2CONHCH_3$
$C_6H_5SO_2NH_2$ . . .	149	31	$C_6H_5SO_2NHCH_3$
$C_6H_5CHOHCOOH$.	118	52	$C_6H_5CHOHCOOCH_3$

It may be observed as an interesting fact that if the elements in a group of the periodic table replace one another in organic compounds, the melting-point usually falls with increasing atomic weight. This behaviour is contrary to that previously mentioned with the halogen derivatives of the elements. The data available are too few to enable the relation to be stated as a general rule ; moreover, as will be seen in the examples quoted below, the halogens are exceptional.

TABLE VI.

Substance.	M.P.	Substance.	M.P.
$(C_6H_5)_2O$	28°	$(C_6H_5)_4C$	282°
$(C_6H_5)_2S$	liquid	$(C_6H_5)_4Si$ . . .	228°
$(C_6H_5)_3N$	127°	$(C_6H_5)_4Sn$ . . .	226°
$(C_6H_5)_3P$	75°	$(C_6H_5)_4Pb$ . . .	224°
$(C_6H_5)_3As$	58°	$C_6H_4F_2(1·4)$ . . .	liquid
$(C_6H_5)_3Sb$	48°	$C_6H_4Cl_2(1·4)$ . .	53°
$(C_6H_5)_3Bi$	78°	$C_6H_4Br_2(1·4)$ . .	89°
C_6H_5COOH . . .	121°	$C_6H_4I_2(1·4)$ . . .	129°
C_6H_5SiOOH . . .	92°		

From these examples of homologous series and replacements we see the highly constitutive nature of fusibility. It seems impossible to define any quantitative relations between this property and composition, and even the qualitative relations mentioned are irregular and of limited application. In order to illustrate more fully the constitutive character of the property we may now turn to isomeric substances.

§ 5. *ISOMERIC COMPOUNDS*

It is rare to find two isomeric compounds of the same melting-point; but, as a rule, a given isomeric change causes the same qualitative alteration in fusibility. Quantitative relations connecting the type of isomerism with the melting-point are as difficult to detect as with replacements. We shall restrict our attention to the qualitative relations of (*a*) structural isomerides, (*b*) stereo-isomerides.

(*a*) *Structural Isomerides.*—There are two general rules relating the type of structure of compounds to their fusibility.

(1) Of two isomeric compounds, that which contains the more symmetrical structure possesses the higher melting-point.

(2) Of two isomeric compounds, that which possesses the more highly branched chain of carbon atoms melts at the higher temperature.

The former of these relations was first noticed by Carnelley [1] and the latter by Markownikoff.[2] To illustrate the influence of symmetry of structure, the following list of aliphatic compounds is given (see Table VII.).

In further illustration of this rule reference may be made to the di- and multi-substituted derivatives of benzene whose fusibilities have been compared by Carnelley and by Marckwald. In most cases of the di-substituted derivatives the para isomeride melts at a higher temperature than the less symmetrical ortho and meta compounds; but for the numerous data in support of this rule and a few exceptions to it, the reader must be referred to the original literature on the subject.

[1] Carnelley, *Phil. Mag.*, [5] 13, 116 (1882) ; see also Watts, *Dictionary of Chemistry*, 3rd Supplement ; Marckwald, *Lehrbuch der Chemie*, Graham-Otto, I., 3, 305 ; Franchimont, *Rec. Pays Bas.*, 16, 142 (1897).

[2] Markownikoff, *Ann.*, 182, 340 (1876), and Marckwald, *loc. cit.*

TABLE VII.

Substance.	M.P.	Substance.	M.P.
$(COOHCH_2)_2CHOH$	155°	$(CH_3)_3C.CH_2OH$	49°
$COOH(CH_2)_2CHOHCOOH$	72·3°	$(CH_3)_2(C_2H_5)COH$	− 12°
$(C_2H_5)_2SO_2$	70°	$CO(C_6H_{13})_2$	30°
$C_2H_5SO.OC_2H_5$	liquid	$CH_3COC_{11}H_{23}$	28°
$C_2H_6CHCOOH$		$CH_3(CH(CH_3)COOH)_2$	127°
$C_2H_5CHCOOH$	190°		
$CH_6CHCOOH$		$CH_3{<}{CH_2COOH \atop C(CH_3)_2COOH}$	85°
$C_2H_7CHCOOH$	174°		
γ. Methyl pimelic acid	56°	β. Ethyl glutaric acid	67°
β. Methyl pimelic acid	49°	α. Ethyl glutaric acid	60°
α. Methyl pimelic acid	54°		

With substances containing two or more benzene nuclei united together the relations are more complex, especially in those which contain "annealed" ring systems. Even in a simple substance like diphenyl the effect of symmetry cannot be clearly followed. The annexed list shows that the di-para substituted compounds of this group melt at a higher temperature than the other isomerides; and this is to be expected, since in these compounds each benzene nucleus is substituted in the most symmetrical manner possible.

TABLE VIII.

Substance.	M.P.	Substance.	M.P.
2·4′ dinitrodiphenyl	93·5°	2·4′ dioxydiphenyl .	160°
2·2′ ,,	124·0	2·2′ ,,	109
4·4′ ,,	233	4·4′ ,,	272
3·3′ ,,	197	3·3′ ,,	123
2·4′ diaminodiphenyl	45	2·4′ dicarboxydiphenyl	251
2·2′ ,,	81	2·2′ ,,	229
4·4′ ,,	122	4·4′ ,,	decomposes at
3·3′ ,,	liquid		high temperature

Turning to the other derivatives we find that the rule of symmetry does not apply. With ortho-para compounds one
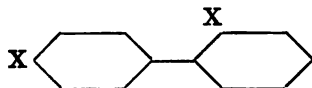
benzene nucleus is substituted symmetrically (para), and the melting-point of this type should lie between those of the di-ortho and di-para substitution products. This conclusion is confirmed by the phenols and carboxylic acids, but is negatived by the amino and nitro compounds.

In determining the relative symmetry of these substances another point of view might be assumed, we might instead consider the symmetry of the molecule as a whole. Thus the ortho-para compounds, being the least symmetrical, should melt at the lowest temperature ; but the agreement between theory and fact would be no better than before. Enough, however, has been said to show the narrowness of the limits which must be set to the rule of symmetry.

The following lists are added to show that the rule may be applied to some of the simpler heterocyclic compounds. With
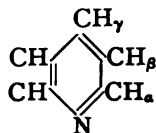
pyridine, substitution in position γ leads to the most symmetical derivatives, and these melt at higher temperatures than the a or β isomerides.

TABLE IX.

Substance.	M.P.	Substance.	M.P.
a. Phenyl pyridine	liquid	a. Pyridone . . .	106°
β. ,, ,,	liquid	β. Oxypyridine . .	124
γ. ,, ,,	77°	γ. Pyridone ($+ H_2O$)	148
a. Amino pyridine	56	Picolinic acid . . .	135–6
β. ,, ,,	64	Nicotinic acid . .	229
γ. ,, ,,	155	Isonicotinic acid . .	304

In pyrazole it is impossible to assign a definite position to the imino hydrogen atom ; the substance may be represented by either—

$$
\begin{array}{ccc}
\underset{3}{CH} \overset{\overset{4}{CH}}{\underset{\underset{2}{N}\!-\!-\!-\!-\underset{1}{NH}}{}} \underset{5}{CH} & \text{or} & \underset{3}{CH} \overset{\overset{4}{CH}}{\underset{\underset{2}{HN}\!-\!-\!-\!-\underset{1}{N}}{}} \underset{5}{CH}
\end{array}
$$
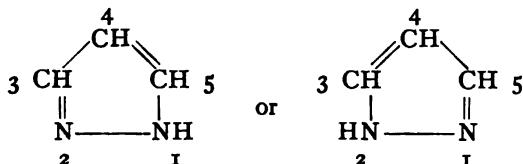
Positions 3 and 5 are identical, and of the mono-substitution products the " 4 " derivatives are the most symmetrical. From the few comparisons which can be made it is clear that these melt at higher temperatures than the " 3 " or " 5 " derivatives.

Substance.	M.P.
3 or 5 phenyl pyrazole	50°
4 „ „	228°
3 or 5 pyrazole carboxylic acid	209°
4 „ „ „	275°
3·5 pyrazole dicarboxylic acid	289°
4·5 „ „ „	260°

The latter pair of substances afford further illustration of the effect of symmetry ; the symmetrical acid

$$
\text{HOOC . C} \overset{\overset{CH}{\diagup\diagdown}}{\underset{\underset{H}{N\;\;N}}{\big|\;\;\big|}} \text{C . COOH}
$$
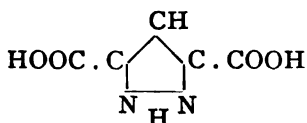
melting at a higher temperature than

$$
\text{CH} \overset{\overset{C . COOH}{\diagup\diagdown}}{\underset{\underset{H}{N\;\;N}}{\big|\;\;\big|}} \text{C . COOH}
$$
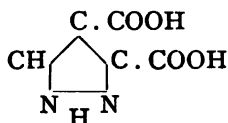
We may now turn to the second of the laws mentioned at the beginning of this section. Markownikoff made the observation that of the isomeric acids $(COOH)_2C_3H_6$ the one with

the most highly branched chain of carbon atoms melts at the highest temperature, and since then other chemists, extending the range of material, have found that the rule holds for a large number of series. Some illustrations are quoted in the table below.

TABLE X.

Substance.	M.P.
$CH_3CH_2CH(OH)COOH$	$44°$
$(CH_3)_2C(OH)COOH$	79
$COOHCH_2CH_2CH_2COOH$	97·5
$COOHCH(CH_3)CH_2COOH$	112
$CH_3CH_2CH(COOH)_2$	111·5
$(CH_3)_2C(COOH)_2$	170
$CH_3(CH_2)_3COOH$	$-58·5$
$(CH_3)_2CHCH_2COOH$	-51
$(C_2H_5)(CH_3)CHCOOH$	liquid
$(CH_3)_3CCOOH$	35
$COOH(CH_2)_4COOH$	148
$COOHCH(CH_3)CH(CH_3)COOH$	192
$(CH_3CH_2)(CH_3)C(COOH)_2$	96
$(CH_3)(C_2H_5)C(COOH)_2$	118
$COOH(CH_2)_5COOH$	105
$COOHCH(CH_3)CH_2CH(CH_3)COOH$ . . .	127
$COOHCH(CH_3)C(CH_3)_2COOH$	151
$CH_3CH_2CH_2CH_2C(COOH)_2$	101
$(CH_3)(CH_2CH_2CH_2)C(COOH)_2$	107
$(CH_3)\left({}^{CH_3}_{CH_3}{>}CH\right)C(COOH)_2$	124

It is not claimed that either the law of symmetry or that of chain branching is without exception. Some exceptions to the former of these rules have been quoted in a previous paragraph, and it may now be noted that the substances shown in the following lists do not fall in with the latter rule. In the three comparisons which are made it is evident that the acid containing the "iso" structure melts at the lower temperature.

TABLE XI.

Substance.	M.P.	Substance.	M.P.
Hydrocinnamic acid $C_6H_5CH_2CH_2COOH$ . .	47°	β. Phenyl isobutyric acid $C_6H_5CH_2CH(CH_3)COOH$	37°
Hydratropic acid $C_6H_5CH(CH_3)COOH$ . .	liquid	Butyric acid $CH_3CH_2CH_2COOH$ . .	−7·9
γ. Phenyl butyric acid $C_6H_5CH_2CH_2CH_2COOH$	51·7	Isobutyric acid $(CH_3)_2CHCOOH$ . . .	−79

In some isomeric substances the two laws clash, and thus exceptions to one or the other are formed. The lists which are quoted below illustrate this antagonism. The members in each series of isomers are arranged according to the degree of branching of the carbon chain; the simplest substances come first, whilst at the end of each list is placed the isomeride with the most highly branched chain.

TABLE XII.

Substance.	M.P.
Adipic acid, $COOH(CH_2)_4COOH$	148°
α methyl glutaric acid, $COOH . CH(CH_3)CH_2CH_2COOH$	76
β methyl glutaric acid, $COOH . CH_2CH(CH_3)CH_2COOH$	86
sym. dimethyl succinic acid $COOH . CH(CH_3)CH(CH_3)COOH$ }	193
as. dimethyl succinic acid, $COOH . C(CH_3)_2CH_2COOH$.	140
Pimelic acid, $COOH(CH_2)_5COOH$	105
$\alpha\alpha'$ dimethyl glutaric acid $COOH . CH(CH_3)CH_2CH(CH_3)COOH$ }	{ 127 and 140
$\alpha\alpha$ dimethyl glutaric acid $COOH . C(CH_3)_2CH_2CH_2COOH$ }	85
$\beta\beta$ dimethyl glutaric acid $COOH . CH_2CH(CH_3)_2CH_2COOH$ }	104
Trimethyl succinic, $COOH . C(CH_3)_2CH(CH_3)COOH$.	151
Suberic acid, $COOH(CH_2)_6COOH$	140
α methyl pimelic acid $COOH . CH(CH_3)CH_2CH_2CH_2CH_2COOH$ }	54
$\beta\beta$ dimethyl adipic acid $COOH . CH_2C(CH_3)_2CH_2CH_2COOH$ }	102
$\alpha\alpha\alpha'$ trimethyl glutaric acid $COOH . C(CH_3)_2CH_2CH(CH_3)COOH$ }	97
$\alpha\beta\beta$ trimethyl glutaric acid $COOH . CH(CH_3)C(CH_3)_2CH_2COOH$ }	88
Tetramethyl succinic acid $COOH . C(CH_3)_2C(CH_3)_2COOH$ }	190

After examining these series it becomes clear that the effect of splitting up the carbon chain is at first subordinate to the influence of symmetry ; thus *a* methyl glutaric and *as*-dimethyl succinic acids are more readily fusible than adipic acid, *aa* and *ββ* dimethyl glutaric acids melt more easily than pimelic acid, and the substituted pimelic, adipic and glutaric acids melt at a lower temperature than suberic acid. When, however, the branching is carried out to greater degree the effect of symmetry may be in turn overcome, and this would account for the relations between trimethyl succinic and pimelic acids. If symmetry and a highly branched carbon chain occur together, the substance melts at a relatively high temperature ; for example, *sym*-dimethyl and tetramethyl succinic acids have the highest melting-point of their respective series.

TABLE XIII.

Substance.	Active.	Externally compensated.	Internally compensated.
Malic acid	100°	130·5°	—
Camphoric acid	187	204	—
Mandelic acid	132·8	118·0	—
Isocamphoric acid	171	191	—
Bromosuccinic acid	173	160	—
Tropic acid	128	117	—
Styceric acid	167	141	—
Benzoyl alanine	297	162	—
Benzoyl tyrosine	162	192	—
Camphor.	175	178	—
Borneol	203	210·5	—
Methyl ethyl phenacyl-sulphonium picrate	125	116	—
Methyl ethyl phenyl-benzyl ammonium bromide . . .	155–6	55–6	—
Erythrite	88	72	126°
Tetra acetyl erythrite . . .	liquid	53	85
Tartaric acid	170°	205	140–3
Dimethyl tartrate	43·3	89·4	111
Diethyl tartrate	liquid	liquid	54
Hydrobenzoin	—	119	134
Diphenyl oxethylamine . .	—	129	163
Diphenyl ethylene diamine .	—	91	120
Xylotrioxyglutaric acid . .	127°	154	152
Hexahydrophthalic acid . .	179–183	215	192

(*b*) *Stereoisomers.*

(1) *Optical Isomerides.*[1]—In the table on p. 206 the melt-ing-points of some optically active substances are compared with those of the inactive compounds, and it is evident that there is no simple rule connecting the fusibility of externally compensated with that of active substances. In many cases it is not known whether the active substance is a true racemate, a mixed crystal, or a conglomerate, and until this is deter-mined it is useless to discuss the matter further. Comparing active with internally compensated substances, we again fail to discover any simple relations.

(2) *Ethylenic Isomerides.* — Michael[2] has established the rule that the maleinoid modification of unsaturated compounds melt lower and are more soluble and volatile than the corre-sponding fumaroid isomers. A few examples are quoted below.

TABLE XIV.

Maleinoid form.			Fumaroid form.
Substance.	M.P.	M.P.	Substance.
Maleic acid	130°	200°	Fumaric acid
Citraconic acid . . .	91	202	Mesaconic acid
Ethyl maleic acid . . .	100	194	Ethyl fumaric acid
Propyl maleic acid . .	94	174	Propyl fumaric acid
Isocrotonic acid . . .	15·5	72	Crotonic acid
Angelic acid	45	64·5	Tiglic acid
Oleic acid	14	51·0	Elaidic acid
Allo - *a* - chlorocinnamic acid	111	137	*a*-chlorocinnamic acid

(3) *Stereoisomerides of the Oxime Type.*—It may be stated that as a rule the syn forms of the aldoximes melt at higher temperatures than the corresponding anti derivatives; but the rule cannot be extended to derivatives of the oximes, since with the ethers and carbanilide derivatives the reverse relations

[1] Walden, *Ber.*, **29**, 1692 (1896).
[2] *J. Pr. Chem.*, [2] **52**, 345 (1895).

are usually found. With ketoximes and hydroximic acids it seems impossible to detect any general relations among the melting-points of the isomeric forms. The following list may be consulted for illustration of what has been said of carbon-nitrogen isomerides.

TABLE XV.

ALDOXIMES AND DERIVATIVES.

Name.	M.P. syn.	Anti.
Benzaldoxime	128°	34°
Mesitylaldoxime	179	124
Anisaldoxime	130·5	61
Benzaldoxime carbanilide	94	74
Cinnamic aldoxime	138·5	64
p. nitrobenzaldoxime	174	129
Anisaldoxime methyl ether	liquid	243
Cuminic-aldoxime carbanilide . . .	93	139

§ 6. *CONCLUSION*

From the brief survey which we have taken of the relations between fusibility and chemical constitution, it is clear that the property is highly constitutive ; indeed, additive relations cannot be detected. Moreover, it will be observed that none of the rules which have been set forth are without exception. Perhaps the most interesting attribute of fusibility is the manner in which it is influenced by the form or symmetry of the molecule ; and this at once suggests that the property is subject to steric influences. Further, it seems probable that steric conditions may make themselves felt in other ways ; for a considerable quantity of evidence can be adduced to show that, other conditions being constant, an increasing tendency to intra-molecular collision lowers the fusion point of the compound ; for example, the cis isomerides of the polymethylene derivatives are more readily fusible than the cis-trans modifications. Some examples of this relation are quoted in the annexed table.

TABLE XVI.

Substance.	M.P. Cis form.	M.P. Cis-trans form.
Trimethylene, 1.2 dicarboxylic acid . .	139°	175°
Trimethylene, 1.2.3 tricarboxylic acid .	150–3	220
Caronic acid	176	213
Hexahydrophthalic acid	192	215
Hexahydroisophthalic acid	162	188
Hexahydroterephthalic acid	161	200
Δ². Tetrahydroterephthalic acid . . .	150	300
Diethyl succino-succinic ester . . .	liquid	65
Dipropyl succino-succinic ester . . .	liquid	86

The relations between the ethylenic isomers may be explained in the same way, since, here again, it is the cis form which is the more readily fusible. Moreover, it is noteworthy that in some alternating homologous series, *e.g.* the mono- and dibasic fatty acids, the most easily fusible member of all is that containing five carbon atoms, and, according to stereo-chemical theory, there is in these substances a marked tendency to intra-molecular collision. But before this hypo-thesis can be finally accepted it must be shown to be in accord with the physical conception of the process of fusion, and this cannot be done until the kinetic theory of solids is developed beyond its present state.

There is no doubt that the most remarkable attribute of fusibility is the alternation seen in homologous series, and as yet no serious explanation of this has been attempted. It may be remarked that Biach[1] claims to have shown that the alternation is due to changes in residual affinity of the succes-sive carbon atoms in the chain; but the statement seems purely speculative. Further knowledge of the physical process of fusion is desirable, and when this is acquired, it is probable that the relations between fusibility and constitution will be worth more serious attention than they have hitherto received.

[1] *Zeit. Phys. Chem.*, **50**, 43 (1905).

CHAPTER VII

BOILING-POINT AND CHEMICAL CONSTITUTION

§ I. *INTRODUCTION*

KOPP,[1] in 1842, was the first to investigate the relations between chemical composition and boiling-point. His first generalisation was that a given change in composition always corresponds to the same change in boiling-point; and following up this idea he calculated the boiling-point effects of carbon and hydrogen in homologous compounds. From his later researches he further deduced that isomeric compounds of equal vapour density (metamers) boil at the same temperature. Schröder,[2] another of the earlier investigators, endeavoured to calculate the average effect of an equivalent of carbon hydrogen and oxygen. In spite of the fact that a controversy [3] on the validity of Schröder's method of calculation arose between these chemists, their conception of the nature of boiling-point seems to have been much the same. Although both laid stress on the additive side of the property, neither considered it to be entirely additive in character; indeed, Schröder definitely stated that constitution must affect the boiling-point. Löwig [4] and Gerhardt,[5] on the other hand, regarded it as purely additive. More recent investigation has shown that the generalisations of these earlier workers [6] are incorrect; but in spite of this

[1] *Ann.*, **41**, 79, 169 (1842).
[2] *Ann.*, **76**, 176 (1850).
[3] *Pogg. Ann.*, **81**, 374 (1850).
[4] *Pogg. Ann.*, **66**, 250 (1845).
[5] *J. Fr. Chem.*, **35**, 300 (1845).
[6] A very good description of the earlier work is given in Gmelin's *Chemistry*, vol. **7**, 55 (1852).

they should not be neglected, since their value lies in the stimulus which they gave to further research. It must also be remembered that many of the difficulties with which Kopp and Schröder had to contend are not encountered by the modern chemist. For instance, methods of accurately determining boiling - points were unknown, so that Kopp was obliged thoroughly to test his method before he could place reliance on the observations. Also the range of material was limited, isomeric compounds were comparatively scarce, and homologous series were only imperfectly known. When these and other circumstances are considered, it seems surprising that Kopp was able to succeed as well as he did.

Before discussing the data which are at present available, we may notice the errors with which they are liable to be contaminated. Frequently data have to be taken from the observations of different chemists, and this may introduce inaccuracies, for it is not always stated by the observer whether the boiling-point is corrected for the length of mercury column out of the vapour. Moreover, in many cases the substance may be scarce and, having been only purified sufficiently to give good analytical results, the sample may boil within three or four degrees. In ordinary determinations of boiling-point the pressure is rarely measured accurately.

The most reliable data are found in researches which have been made expressly to find the relations of vapour pressure and temperature, such as those of Ramsay and Young, Naumann, and others; but these, unfortunately, do not deal with the range of material that is necessary.

§ 2. *INORGANIC SUBSTANCES*

Carnelley has shown that, like fusibility, the boiling-point of an element is related to its position in the periodic system. It cannot be stated as a general rule that increase in atomic weight is accompanied by an increase in boiling-point. The series of elements in the vertical columns of the periodic table show characteristic behaviour. As a rule, the families of non-metals increase in boiling-point with rising atomic weight.

TABLE I.

	B.P. (abs.).		B.P. (abs.).		B.P. (abs.).
Nitrogen . .	78°	Oxygen . .	90°	Fluorine .	86°
Phosphorus .	363	Sulphur . .	717	Chlorine. .	240
Arsenic . .	700	Selenium .	963	Bromine .	336
Antimony .	1713	Tellurium .	1663	Iodine . .	457
Bismuth . .	1708				

The argon group shows the same behaviour—

Helium . . . . . . 4·5° (abs.)
Argon . . . . . . 86·9° ,,
Krypton . . . . . . 121·3° ,,
Xenon . . . . . . 164° ,,

On the other hand, the reverse change is observed with the alkali metals and heavy metals.

B.P. (abs.).   B.P. (abs.).
Sodium . . . 1013   Magnesium . . 1373°
Potassium . . 940   Zinc . . . . 1200°
                       Cadmium . . 1045°
                       Mercury . . . 630°

On passing through the elements in a period the boiling-points are seen at first to rise to a maximum about the middle of the period, and then, after a sudden fall, to decrease slightly.

ORGANIC COMPOUNDS

§ 3. *ISOMERIC SUBSTANCES*

Kopp [1] at first maintained that isomeric substances should boil at the same temperature. This conclusion was based upon only a few comparisons, and at a later period, when more

[1] *Ann.*, **50**, 142 (1844).

material was available, objections to it were raised. It was soon found that chemical structure has a greater influence on volatility than had been imagined. Dittmar's[1] careful measurements of the vapour pressures of ethyl formate and methyl acetate made it quite clear that at any rate these isomerides have not the same degree of volatility.

TEMPERATURES OF EQUAL VAPOUR PRESSURES

Ethyl formate	$20°$	$26°$	$33°$	$43°$	$53°$
Methyl acetate	$21·7°$	$27·8°$	$34·7°$	$44·5°$	$54·4°$

Wanklyn[2] also showed that ethyl valerate and amyl acetate boil at different temperatures, and Naumann,[3] as will be described later, found a similar divergence in boiling-point with other isomerides. These and other observations[4] of a like character caused Kopp to modify his original idea, and at present it may be stated in a very much restricted form: " Isomeric substances of a similar chemical nature and possessing a similar structure have almost the same boiling-points."

From this generalization the character of the property is evident. Since isomerides of widely different chemical nature have quite different boiling-points, it is clear that the property is to a certain degree constitutive. On the other hand, the presence of additive characteristics may be inferred from the closeness in boiling temperature of isomerides of similar constitution. The subjoined tables show the boiling-points of a few isomerides, those in Table II. being of closely allied structures; whilst the comparisons shown in Table III. are made with substances of quite different constitution.

[1] *Annalen. Suppl.*, **6**, 313 (1868).
[2] *Annalen*, **137**, 38 (1866).
[3] *Ber.*, **7**, 173, 206 (1874) ; *Ber.*, **1**, 30 (1898).
[4] Dobriner, *Ann.*, **243**, 1 (1888) ; Schumann, *Wied. Ann.*, **12**, 40 (1881); Linnemann, *Ann.*, **162**, 39 (1872) ; Schreiner, *Ber.*, **11**, 179 (1878); see also the effect of chain branching and symmetry.

TABLE II.

KETONES.

Substance.	B.P.	Substance.	B.P.
$(C_2H_5)_2CO$	103° ⎱	$C_2H_5COCH(CH_3)_2$ . . .	114° ⎱
$CH_3COC_3H_7$ . . .	102 ⎰	$CH_3COCH_2CH(CH_3)_2$ . .	115 ⎰
$(C_5H_{11})_2CO$ . . .	226 ⎱	$C_2H_5COC_3H_7$	122·4 ⎱
$CH_5COC_{13}H_{19}$ . .	225 ⎰	$CH_3COC_4H_9$	127 ⎰
$(C_6H_{13})_2CO$ . . .	263 ⎱	$(C_3H_7)_2CO$	144 ⎱
$CH_3COC_{11}H_{23}$ . . .	263 ⎰	$CH_3COCH_2CH_2CH(CH_3)_2$	144 ⎰

ETHERS.[1]

$CH_3OC_3H_7$	38·9 ⎱	$(C_4H_9)_2O$	141 ⎱
$(C_2H_5)_2O$	35 ⎰	$CH_3OC_7H_{15}$	150 ⎰
$(C_3H_7)_2O$	86·0 ⎱	$C_2H_5OC_6H_{13}$	134-7 ⎱
$C_2H_5OC_4H_9$	91·4 ⎰	$C_4H_9OC_7H_{15}$	205·7 ⎰
$CH_3OC_5H_{11}$	91·3 ⎰	$C_3H_7OC_8H_{17}$	207 ⎰
$(C_2H_5)_2S$	93		
$CH_3SC_3H_7$	93-5		

PHENOLIC ETHERS.[2]

Substance.	B.P.	B.P.	Substance.
$C_6H_5OC_2H_5$ . . .	172°	175°	$CH_3C_6H_4OCH_3(1·4)$
$C_6H_5OC_3H_7$ . . .	190·5	189·8	$CH_2C_6H_4OC_2H_5(1·4)$
$C_6H_5OC_4H_9$ . . .	210·3	210·4	$CH_3C_6H_4OC_3H_7(1·4)$
$C_6H_5OC_8H_{17}$ . . .	282·8	283·3	$CH_3C_6H_4OC_7H_{15}(1·4)$

ESTERS.

Substance.	B.P.	Substance.	B.P.
Methyl acetate . . .	57·5°	Butyl formate . . .	107°
Ethyl formate . . .	54·4	Propyl acetate . . .	102
		Ethyl propionate . .	98·8
Propyl formate . . .	81	Methyl butyrate . .	102·3
Ethyl acetate . . .	77		
Methyl propionate . .	79·5	Octyl acetate . . .	210
		Heptyl propionate .	208
Hexyl formate . . .	153·6	Hexyl butyrate . .	205
Amyl acetate . . .	148	Amyl valerate . . .	204
Butyl propionate . .	146	Butyl hexylate . . .	204·3
Propyl butyrate . . .	143	Propyl heptylate . .	206·4
Ethyl valerate . . .	144	Ethyl octylate . . .	206
Methyl hexylate . .	149·6		

[1] Dobriner, *Ann.*, **243**, 1 (1888).　　　[2] Pinnette, *Ann.*, **243**, 32 (1888).

TABLE II.—*continued.*

ALDEHYDES AND KETONES.

Substance.	B.P.	B.P.	Substance.
C_2H_5CHO . . .	49°	56·5°	CH_3COCH_3
n. C_3H_7CHO . .	75	81	$CH_3COC_2H_5$
n. C_4H_9CHO . .	103	102	$CH_3COC_3H_7$
n. $C_5H_{11}CHO$ . .	128	127	$CH_3COC_4H_9$
n. $C_6H_{13}CHO$ . .	155	151·2	$CH_3COC_5H_{11}$

Although the last three terms in the aldehydes and ketones agree fairly well, there is considerable difference in the simpler

TABLE III.

Substance.	B.P.	B.P.	Isomeric Substance.
C_2H_5OH	78·3°	−23°	CH_3OCH_3
$CH_3(CH_2)_4CH_2OH$ . .	157	86	*n.* $C_3H_7OC_3H_7$
C_4H_9SH	98	91	$C_2H_5SC_2H_5$
CH_3CHO	20·8	12·5	CH_2—CH_2 (O bridge)
C_2H_5CHO	49	35	CH_3—CH—CH_2 (O bridge)
$(CH_3CH_2CH_2)O$ . . .	50	49	C_2H_5CHO
$(CH_3CH_2CH_2CH_2)O$ . .	57	75	C_3H_7CHO
$(CH_3CH_2CH_2CH_2CH_2)O$.	82	103	C_4H_9CHO
CH_3NO_2	101	−12	CH_3ONO
$C_2H_5NO_2$	113	+16	C_2H_5ONO
$C_2H_5SO_2OC_2H_5$ . . .	213	161	$(C_2H_5O)_2SO$
CH_3CN	81·6	59	CH_3NC
C_2H_5CN	98	79	C_2H_5NC
$CH_3CH=CHCCOH$.	180	87–9	$CH_3COCOCH_3$
$CH_2=CH(CH_2)_2COOH$.	187	108	$CH_3COCOC_2H_5$
$CH_3COCH_2COCH_3$ . .	137	108	$CH_3COCOC_2H_5$
$CH_3COCH_2CH_2COCH_3$	194	158	$CH_3COCH_2COC_2H_5$
$(CH_3)_2C.OHCHO$ . .	137	155	$(CH_3)_2CH.COOH$
$CH_3.C{\equiv}C.CH_3$ . . .	27	−5	$CH_2=CH—CH=CH_2$
$CH_2CH_2CH_2CH_2CH_2$.	50	39	$CH_3CH_2CH_2CH=CH_2$
$CH_2OH(CH_2)_2CH_2OH$.	202	65	$CH_3CH_2OOCH_2CH_3$
CH_2ClCH_2COCl . . .	143–5	120	$CH_3COCHCl_2$
$CH_2OH\ CH_2Cl$ . . .	128	60	CH_3OCH_2Cl

members.   In the esters, too, those of formic acid do not fit
in well with the higher acids.   Such abnormalities are often
found with the simple members of a series, and these are
usually ascribed to association.   When the chemical natures
of two isomerides are different, the boiling-points nearly
always exhibit a wide divergence.

Iso-compounds.—A few attempts have been made to trace
the effect of varying structure on the volatility of isomerides.
It is interesting to find that boiling-point, like fusibility, is
influenced by the form of the atomic chain in the molecule.
The researches of Hinrichs,[1] Naumann,[2] and Menschutkin[3]
have clearly shown that—

"*Of two isomeric substances that with the more highly branched
chain of atoms is the more volatile.*"

It cannot be denied that there are exceptions to this, the
most notable being the derivatives of benzene, in which
increasing substitution leads to decrease in volatility.   Table
IV. contains some examples which are chosen at random from
different classes of compounds.

TABLE IV.

Substance.	Boiling-point.
$CH_3(CH_2)_2CH_2OH$	116·8
$(CH_3)_2CHCH_2OH$.	108·4
$(CH_3)(C_2H_5)CH . OH$.	99
$(CH_3)_3C . OH$	83
$CH_3(CH_2)_2CH_2NH_2$	76
$(CH_3)_2CHCH_2NH_2$	68
$(CH_3)_3CNH_2$	43
$CH_2=CH—CH=CH—CH_3$.	42
$CH_2=CH - C=CH_2$ . . . . $\quad\quad\mid$ $\quad\quad CH_3$	35

[1] *Jahresbericht,* 1868, p. 80.
[2] *Ber.,* **7,** 173, 206 ; **31,** 30 (1898).
[3] *Ber.,* **30,** 2784 (1898); **31,** 313 (1899).

TABLE IV.—*continued.*

Substance.	Boiling-point.
$(CH_3CH_2CH_2)_2CO$	144
$\left(\begin{matrix}CH_3\\CH_3\end{matrix}>CH\right)_2 CO$	124
$CH_3(CH_2)_4COOH$	205
$(CH_3)_2CH(CH_2)_2COOH$	198
$(CH_3)_2(C_2H_5)C.COOH$	187
$CH_2CH_2CH_2CH_2CH_2$ . . . . (with O bridge)	82
$CH_2CH_2CH_2CH.CH_3$ . . . . . . (with O bridge)	77
$(C_2H_5)_2CHI$	145
$\begin{matrix}CH_3\\C_3H_7\end{matrix}>CHI$	144
$\begin{matrix}CH_3\\(CH_3)_2CH\end{matrix}>CHI$	138
$CH_3(CH_2)_4CH_3$	71
$CH_3CH(C_2H_5)_2$	64
$CH_3CH_2CH_2CH(CH_3)_2$	62
$(CH_3)_2CHCH(CH_3)_2$	58
$CH_3CH_2C(CH_3)_3$	49
$CH_3CO(CH_2)_3CH_3$	127
$CH_3COC(CH_3)_3$	106
$CH_3(CH_2)_5COOH$	223
$CH_3(C_4H_9)CHCOOH$	210
$CH_3(C_2H_5)_2C.COOH$	208
$CH_3(CH_2)_3CH_2Br$	128
$(CH_3)_2CH.CH_2.CH_2Br$	120
$C_2H_5NH—NHC_2H_5$	97
$(C_2H_5)_2N.NH_2$	85

Symmetry.—It has been further claimed by Earp[1] that the volatility of a liquid is influenced by the symmetry of molecular structure, and that substances with unsymmetrical molecules boil at a higher temperature than more symmetrical isomers.

[1] *Phil. Mag.*, [5] **35**, 462 (1893).

This is probably true, but the evidence which can be adduced
in favour of it is only very scanty, and is often liable to
interpretation in other ways.   On comparing the boiling-points
of various isomeric oxygen compounds, Naumann found that
the position of the oxygen in the molecule influences the
volatility.   Substances which contain oxygen at the end of
the chain boil higher than isomers in which that element
lies near the centre.   At that time Naumann merely employed
this with his researches on branched chain isomers to refute
Kopp's law that isomeric compounds of the same nature must
boil at the same temperature.   The data may now be
employed to show the effect of symmetry.   The examples
appended in Table V. show that substances in which the
oxygen is symmetrically placed[1] boil at a lower temperature
than isomers of an unsymmetrical structure.

TABLE V.

Substance.	Boiling-point.
$CH_3CH_2CH_2CH_2OH$	$116·8°$
$CH_3CH_2CHOH . CH_3$	$99·9$
$CH_3CH_2CH_2CH_2CH_2OH$ . . .	137
$CH_3CH_2CH_2CH(OH)CH_3$ . . .	118
$CH_3CH_2CH(OH)CH_2CH_3$ . . .	112
$CH_3CH_2CH_2OCH_3$	37
$CH_3CH_2OCH_2CH_3$	$35·5$
$CH_3CH_2CH_2CH_2OCH_2CH_3$ . .	92
$CH_3CH_2CH_2OCH_2CH_2CH_3$ . .	86
$CH_3(CH_2)_5CH_2OCH_3$	$149·8$
$CH_3(CH_2)_2CH_2OCH_2(CH_2)_2CH_3$.	141

Marckwald[2] has drawn attention to a similar relationship
in halogen derivatives.   The same investigator has observed
that when two or more atoms of halogen are present, the
boiling-point is influenced by the position of these with regard
to one another ; the closer they lie together, the lower is the
boiling-point.   The same effect can be seen with other
substituting groups such as hydroxyl, carbonyl, and carboxyl.

[1] See also Dobriner, *Ann.*, **243**, 1 (1888).
[2] *Beziehungen zwischen den Siedepunkte und der Zusammensetzung*,
Berlin, 1888.

TABLE VI.

Substance.	B.P.
CH₃CH(OH)CH(OH)CH₃	184°
CH₃CH₂CH(OH)CH₂OH	192
CH₃CH(OH)CH₂CH₂OH	207
CH₂(OH)CH₂CH₂CH₂OH	202
CH₃C(COOC₂H₅)₂CH₃	195
CH₃CH₂CH(COOC₂H₅)₂	200
CH₃CH(COOC₂)CH₂(COOC₂H₅)	218
CH₂(COOC₂H₅)CH₂CH₂(COOC₂H₅)	237
CH₃COCOC₂H₅	108
CH₃COCH₂COCH₃	137
CH₃COCOC₃H₇	128
CH₃COCH₂COC₃H₅	158
CH₃COCH(CH₃)COCH₃	169
CH₃COCH₂CH₂COCH₃	194
CH₃CH(OH)CH₂OH	188
CH₂(OH)CH₂CH₂OH	216
CH₃CH(OH)CH₂CH(OH)CH₃	177
CH₃CH₂CH(OH)CH(OH)CH₃	187
CH₃CH(OH)CH₂CH₂CH₂OH	219
CH₂OHCH₂CH₂CH₂CH₂OH	260
CH₃CHNH₂CH₂NH₂	119
NH₂CH₂CH₂CH₂NH₂	135
CH₃CCl₂CH₃	70
CH₃CH₂CHCl₂	98
CH₂ClCH₂CH₂Cl	119

Some of the series quoted in the above table show how the effect of symmetry may be overcome by the influence of substitution. Thus propylidene chloride, although unsymmetrical, boils at a lower temperature than the symmetrical trimethylene chloride, and the unsymmetrical 3.4 dihydroxypentane is more volatile than 1.5 pentylene glycol. When the substitution is the same, the effect of symmetry becomes apparent, as with 2.2 dichloropropane and propylidene chloride, or with the esters of dimethyl and ethyl malonic acids.

The evidence put forward to illustrate these generalizations is collected from the simpler compounds of the fatty series. When more complicated substances are examined, many exceptions are met with, hence the relationships described must be regarded as merely rules of very limited scope. In concluding these remarks on isomeric substances, it may be mentioned that, according to Michael,[1] the maleinoid form of ethylene isomerides is always more volatile than the fumaroid variety.

Having discussed the constitutive side of this property, we may now turn to its additive characteristics. These are best illustrated by homologues.

§ 4. *HOMOLOGUES*

At first, Kopp was of the opinion[2] that in all homologous series the average difference in boiling-point between two successive members was $19°$. As illustrations, he quoted the alcohols, acids, some esters, and nitriles, whilst later Schmidt and Fieberg[3] added the series of fatty ketones. Kopp's[4] later researches showed that in many cases the difference is greater than $19°$, and he modified his views accordingly. Church[5] agreed with Kopp that the difference for CH_2 is constant throughout any given series, but he pointed out that the value is different in different classes of compounds. As organic chemistry developed, and more homologous series became known, Kopp's rule became disputed. Schorlemmer[6] pointed out that in the fatty hydrocarbons and their derivatives the value for CH_2 falls off continuously on ascending the series, and Zwicke and Franchimont[7] discovered the same

[1] *J. Pr. Chem.*, [2] **52**, 345 (1895).

[2] *Ann.*, **41**, 86 and 169 (1842).

[3] *Ber.*, **6**, 498 (1873).

[4] *Ann.*, **50**, 71 (1844) ; **55**, 166 (1845) ; **64**, 212 (1847) ; **67**, 356 (1848) ; **76**, 180 (1850) ; **94**, 251 (1855) ; **95**, 121 and 307 (1855) ; **96**, 1, 153, 303, 330 (1855) ; **78**, 265, 367 (1856) ; **100**, 19 (1856).

[5] *Chem. News*, **1**, 205 (1859).

[6] *Ann.*, **161**, 281 (1872); **170**, 150 (1878); *Chem. News*, **25**, 101 (1872) ; *Ber.*, **4**, 359, 564 (1871) ; **7**, 1131 (1874).

[7] *Ann.*, **164**, 333 (1872).

behaviour with fatty acids and their esters.[1]   Table VII. gives examples in illustration of this decreasing effect; it also

TABLE VII.

ALDEHYDES.

Substance.	B.P.	Diffce.	Substance.	B.P.	Diffce.
CH_3CHO	20·8°	28·2	n. C_4H_9CHO	103	25
C_2H_5CHO	49	26	n. $C_5H_{11}CHO$	128	27
n. C_3H_7CHO	75	28	n. $C_6H_{13}CHO$	155	
n. C_4H_9CHO	103				

KETONES.

Substance.	B.P.	Diffce.	Substance.	B.P.	Diffce.
CH_3COCH_3	56·5	2×23·2	n. $C_4H_9COC_4H_9$	182	2×22
$C_2H_5COC_2H_5$	103	2×20·5	n. $C_5H_{11}COC_5H_{11}$	226	2×18·5
n. $C_3H_7COC_3H_7$	144	2×19	n. $C_6H_{13}COC_6H_{13}$	263	
n. $C_4H_9COC_4H_9$	182				

METHYL KETONES.

Substance.	B.P.	Diffce.	Substance.	B.P.	Diffce.
CH_3COCH_3	56·5°	24·5	$CH_3COC_6H_{13}$	171°	22
$CH_3COC_2H_5$	81	21	$CH_3COC_7H_{15}$	193	18
$CH_3COC_3H_7$	102	25	$CH_3COC_8H_{17}$	211	14
$CH_3COC_4H_9$	127	24	$CH_3COC_9H_{19}$	225	22
$CH_3COC_5H_{11}$	151	20	$CH_3COC_{10}H_{21}$	247	16
$CH_3COC_6H_{13}$	171		$CH_3COC_{11}H_{23}$	263	

HALOGEN DERIVATIVES.

Substance.	B.P.	Diffce.	Substance.	B.P.	Diffce.
CH_3I	42·5°	29·5	CH_3Br	4·5°	33·5
C_2H_5I	72	30	C_2H_5Br	38	33
C_3H_7I	102	29	C_3H_7Br	71	30
C_4H_9I	131	24·4	C_4H_9Br	101	28
$C_5H_{11}I$	155·4	26	$C_5H_{11}Br$	129	27
$C_6H_{13}I$	181·4	22·4	$C_6H_{13}Br$	156	22
$C_7H_{15}I$	203·8	21·7	$C_7H_{15}Br$	178	21
$C_8H_{17}I$	225·5		$C_8H_{17}Br$	199	

HYDROCARBONS.

Substance.	B.P.	Diffce.	Substance.	B.P.	Diffce.
CH_4	−162°	78	$C_{10}H_{22}$	173°	21·5
C_2H_6	−84	39	$C_{11}H_{24}$	194·5	19·5
C_3H_8	−45	46	$C_{12}H_{26}$	214	20
C_4H_{10}	+1	37	$C_{13}H_{28}$	234	18·5
C_5H_{12}	38	33	$C_{14}H_{30}$	252·5	18
C_6H_{14}	71	27·4	$C_{15}H_{32}$	270·5	17
C_7H_{16}	98·4	27·1	$C_{16}H_{34}$	287·5	15·5
C_8H_{18}	125·5	24	$C_{17}H_{36}$	303	14
C_9H_{20}	149·5	23·5	$C_{18}H_{38}$	317	13
$C_{10}H_{22}$	173		$C_{19}H_{40}$	330	

[1] Also Linnemann, *Ann.*, **162**, 39 (1872).

TABLE VII.—*continued*.

AMINES.

Substance.	B.P.	Diffce.	Substance.	B.P.	Diffce.
CH_3NH_2 . . .	$-6°$	24	$C_7H_{15}NH_2$ . .	155	25
$C_2H_5NH_2$	18	21	$C_8H_{17}NH_2$ . .	180	15
$C_3H_7NH_2$ . .	49	27	$C_9H_{19}NH_2$ . .	195	23
$C_4H_9NH_2$ . .	76	27	$C_{10}H_{21}NH_2$ . .	218	12
$C_5H_{11}NH_2$ . .	103	27	$C_{11}H_{23}NH_2$ . .	233	16
$C_6H_{13}NH_2$ . .	130	25	$C_{12}H_{25}NH_2$ . .	249	16
$C_7H_{15}NH_2$ . .	155		$C_{13}H_{27}NH_2$ . .	265	

CYCLO PARAFFINS.

	B.P.	Diffce.		B.P.	Diffce.
C_2H_6	$-35°$	46	C_6H_{12} . . .	81	36
C_4H_8	$+11$	38	C_7H_{14} . . .	117	31
C_5H_{10}. . . .	49	32	C_8H_{16} . . .	148	23
C_6H_{12}. . . .	81		C_9H_{18} . . .	171	

includes some series where the difference remains nearly constant.

This decreasing effect of additional CH_2 is found in many other series, and it is now generally accepted as the normal behaviour of homologues.

Quantitative Relations.—Many attempts have been made to give a quantitative expression to the relations between the boiling-points of the members in homologous series. Some of the formulæ proposed [1] connect the boiling-point with the number of atoms in the molecule, but they are not very successful. Walker [2] advocates the formula—

$$T = aM^b$$

where T is the absolute boiling-point, M the molecular weight, and a and b are constants for any given series. When applied

[1] Goldstein, *Journ. Russ. Chem. Soc.*, 11, 154 (1879); *Ber.*, 12, 689 and 851 (1879); Mills, *Phil. Mag.*, [5] 17, 180 (1884); Groshans, *Ber.*, 5, 625, 689 (1872); 6, 519, 523, 1079 (1873); 1296, 1355 (1873); see also Pictet, *Compt. Rend.*, 88, 1315 (1879); Burden, *Phil. Mag.*, [4] 41, 528 (1872).

[2] *Journ. Chem. Soc.*, 65, 193 (1894).

to the ethers, fatty acids, hydrocarbons and normal alkyl-chlorides it gives good results, especially with the ethers where the average divergence of the calculated boiling-point from that of experiment is only one per cent. Boggio-Lera[1] recommends the expression —

$$T = a\sqrt{M + b}$$

where T is the absolute boiling temperature, M the molecular weight, and a and b are constants. He claims that this fits all homologous series of the normal type CH_3 —$(CH_2)_2$ —R.

Ramage[2] employs a somewhat similar formula—

$$T = a[M(1 - 2^{-n})]^{\frac{1}{3}}$$

where a is a constant and n is the number of carbon atoms in the molecule. S. Young[3] has pointed out that the difference in boiling-point between two successive homologues may be regarded as a function of the absolute temperature. Thus—

$$\Delta = \frac{144 \cdot 86}{T^{0 \cdot 0148\sqrt{T}}}$$

where Δ is the difference between the boiling-point T of any homologue and that of the next higher member in the series. The table on p. 224 shows the accuracy with which the boiling-points of the paraffins may be calculated by means of this formula.

When the values of Δ in other homologous series are plotted out against the absolute temperature, almost the same curve is obtained as with the paraffins. The lower members of the series show the wider divergence between the experimental and calculated values, and this may be explained either by molecular association or by the fact that the simpler compounds do not contain the group —CH_2—CH_2—CH_2—, and so

[1] *Gazz. Chim. Ital.*, **29**, 1, 441 (1899).

[2] *Proc. Camb. Phil. Soc.*, **12**, 445 (1904).

[3] Address to the chemical section of the British Association (1904); also *Phil. Mag.*, **9**, 1–19 (1905).

TABLE VIII.

Substance.	Absolute boiling-point.		
	Observed.	Calculated.	Difference, obs. and calc.
CH_4	108·3	106·75	− 1·55
C_2H_6	180·0	177·7	− 2·3
C_3H_8	228·0	229·85	+ 1·85
C_4H_{10}	274·0	272·6	− 1·4
C_5H_{12}	309·3	309·4	+ 0·1
C_6H_{14}	341·95	341·95	0
C_7H_{16}	371·4	371·3	− 0·1
C_8H_{18}	398·6	398·1	− 0·5
C_9H_{20}	422·5	422·85	+ 0·35
$C_{10}H_{22}$	446·0	445·85	− 0·15
$C_{11}H_{24}$	467·0	467·35	+ 0·35
$C_{12}H_{26}$	487·5	487·65	+ 0·15
$C_{13}H_{28}$	507·0	506·8	− 0·2
$C_{14}H_{30}$	525·5	525·0	− 0·5
$C_{15}H_{32}$	543·5	542·3	− 1·2
$C_{16}H_{34}$	560·5	558·85	− 1·65
$C_{17}H_{36}$	576·0	574·7	− 1·3
$C_{18}H_{38}$	590·0	589·9	− 0·1
$C_{19}H_{40}$	603·0	604·5	+ 1·5

are not really members of the series. The next table is added to show how this expression may be used to calculate the boiling-points of a number of homologous series. The figures given apply only to derivatives containing C_3 and upwards. The table is divided into two parts, the first of which contains the data from non-associated and the second from associated compounds. It will be seen that the discrepancy between theory and practice is much greater with the latter class of substance.

Young's formula may, therefore, be employed to calculate the boiling-point of any unassociated organic compound containing more than three carbon atoms, provided of course that the boiling-point of the next homologue is known. The error is generally about one degree.

Having now considered the replacement of hydrogen by CH_2 in homologous series, we may turn to Substitution.

TABLE IX.

UNASSOCIATED LIQUIDS.

Series.	No. of values of Δ.	Mean diff. calc.-obs.	Series.	No. of values of Δ.	Mean diff. calc.-obs.
Alkyl chlorides .	5	− 1·04	Paraffins . . .	17	− 0·22
,, bromides .	5	− 1·25	Isoparaffins . .	2	+ 0·57
,, iodides .	3	− 1·0	Toluene, etc. .	3	+ 0·68
Olefines—			Ethers . . .	13	+ 1·12
CH₂=CHR .	3	− 2·35	Aldehydes . .	4	+ 1·3
RHC=CHR′	3	+ 0·5	Hydrosulphides	1	− 0·5
Polymethylenes .	2	− 3·85	Amines . . .	4	+ 1·7
			Esters . . .	67	+ 1·53

ASSOCIATED SUBSTANCES.

Cyanides . . .	4	+ 2·9	Ketones . . .	3	+ 2·85
Nitro methane, etc.	1	+ 3·85	Fatty acids . .	7	+ 1·58
			Fatty alcohols .	5	+ 5·24

§ 5. *REPLACEMENTS*

Following Kopp's rule that a given change in constitution is always accompanied by the same change in boiling-point, chemists have studied a great number of replacements, and many have attempted to state these in a quantitative form. Some of these replacements are collected in Table X. The atoms or groups involved in the change are shown, together with a typical case of the replacement, and in the last column the effect of the exchange on the boiling-point is given.

TABLE X.

Replacement of—	Typical case.	Effect on boiling-point.
Hydrogen by chlorine in a methyl group [1]	CH₃COOH→CH₂ClCOOH →CHCl₂COOH→CCl₃COOH	Continual rise, which falls off with increasing number of halogen atoms.

[1] Henry, *Ber.*, **6**, 734, 962 (1873).

TABLE X.—*continued.*

Replacement of—	Typical case.	Effect on boiling-point.
Hydrogen by chlorine in a methyl group of a chloro derivative [1]	CCl_3—CH_3→CCl_3—CH_2Cl →CCl_3—$CHCl_2$→CCl_3—CCl_3	Continual ris which falls with increasi number of hal gen atoms.
in nitriles [2]	CH_3CN→CH_2ClCN →$CHCl_2CN$→CCl_3CN	Rise with the fi replacement, a then continuo fall.
Hydrogen by bromine in halogen derivatives of ethane or ethylene [3]	CH_3—$CHBrCl$→ CH_2—CBr_2Cl	Rise; greate when bromi enters near hal gen.
Chlorine by bromine [4] in fatty and aromatic compounds	$CH_3CH_2CH_2Cl$ →$CH_3CH_2CH_2Br$	Rise of about 2 throughout.
Chlorine by fluorine [5] .	—	Fall.
Hydrogen by hydroxyl [6] in paraffins . . .	$(CH_3)_3CH$→$(CH_3)_3C$. OH	⎫
in alcohols. . . .	CH_3 . CH_2OH→CH_2OHCH_2OH	⎬ Rise of abou $100°$.
in aldehydes . . .	CH_3CHO→CH_3COOH	⎪
in halogen compounds	CH_2BrCH_3→CH_2BrCH_2OH	⎭
H_2 by oxygen [7] in hydrocarbons . .	$CH_3CH_2C_2H_5$→$CH_3COC_2H_5$	Rise of about 7
in alcohols. . . .	$C_6H_5CH_2OH$→C_6H_5COOH	Rise of about 4
in ethers	$CH_3CH_2OCH_2CH_3$→$CH_3CH_2OCOCH_3$	Rise of about 4
in alkylhalides . .	$C_2H_5CH_2Br$→C_2H_5COBr	Rise of about 3
in nitriles	CH_3CH_2CN→CH_3COCN	Fall.
H by CH_3 [8] in pyridine [9] . . .	Picoline→Lutidine	Rise of about 2
in amines [9]. . . .	$C_6H_5NHCH_3$→$C_6H_5NHC_2H_5$	Rise of about

[1] Städel, *Ber.*, 11, 746 (1878); 13, 839 (1880); 15, 2550 (1882).

[2] Henry, *Ber.*, 6, 734, 962 (1873).

[3] Denzel, *Ann.*, 195, 215 (1879).

[4] Denzel (*loc. cit.*); Marckwald, *Beziehungen zwischen den Siedepunkten und der Zusammensetzung*, Berlin, 1888; see, however, Kopp, *Ann.*, 98, 265 (1856); and Berthelot, *Ann. Chim. Phys.*, [3] 48, 323 (1856).

[5] Swarts, *Chem. Central Blatt.*, I., 14, 1903.

[6] Marckwald (*loc. cit.*); see, however, Cohn, *J. Pr. Chem.*, 50, 38 (1894), for the effect of OH on alcohols.

[7] Henry, *Ber.*, 6, 734 (1873).

[8] See § 4.

[9] Church, *Chem. News*, 1, 205 (1859).

Replacement of—	Typical case.	Effect on boiling-point.
in amides [1] . . .	$CH_3CONH_2 \rightarrow CH_3CONHCH_3$	Fall of 30°.
in α diketones [2] . .	$CH_3COCOCH_3 \rightarrow CH_3COCOC_2H_5$	Rise of 20°.
in aromatic hydrocarbons [3]	$C_6H_4(CH_3)_2 \rightarrow C_6H_3(CH_3)_3$	Rise of about 26°.
O by S		
in carbonates [4] . .	$CO(OC_2H_5)_2 \rightarrow CO(OC_2H_5)(SC_2H_5)$	Rise.
in other sulphur compounds [5]	—	Rise.
OH by SH		
in alcohols [5] . . .	$CH_3CH_2CH_2OH \rightarrow CH_3CH_2CH_2SH$	Fall.
Unsaturation		
in halogen derivatives [6]	$CH_2Cl—CH_2Cl \rightarrow CHCl=CHCl$	Fall.
in hydrocarbons [7] .	$C_4H_{10} \rightarrow C_4H_6$	Rise.
OH by NH₂		
in aromatic compounds [7]	—	Scarcely any change.
C by Si [8]		
in carbon compounds .	$C(CH_3)_4 \rightarrow Si(CH_3)_4$	Rise.
in halogen compounds	$CCl_4 \rightarrow SiCl_4$	Fall.

Whilst studying the above table it must be remembered that just as Kopp's rule is only a first approximation to the truth so also are these relations. We have seen that in homologous series the effect of replacing hydrogen by methyl falls off with increasing molecular weight, and it may now be remarked that the same behaviour can be clearly seen with other replacements.[9]

A closer study of Table XI., p. 228, will show that the rate of decrease in the replacement values becomes less in ascending each series, so that it is conceivable that with the very high members the replacement would assume a constant value.

[1] Schmidt, *Ber.*, **36**, 2459 (1903).
[2] Cohn, *J. Pr. Chem.*, **50**, 38 (1894).
[3] Kopp, *Ann. Suppl.*, **5** (1867).
[4] Carnelley, *Phil. Mag.*, 1867 (1879).
[5] Earp, *Phil. Mag.*, [5] **35**, 458 (1893).
[6] Sabanejeff, *Journ. Russ. Chem. Soc.*, **12**, 48.
[7] Marckwald (*loc. cit.*).
[8] Henry, *Bull. Acad. Roy. Belg.*, 187 (1906).
[9] See Young, *British Association Report* (1904).

TABLE XI.

REPLACEMENT OF HYDROGEN BY BROMINE.

Paraffins.	Boiling-point.	Replacement value.	Boiling-point.	*n.* Alkyl bromides.
CH_4	$-162°$	166·5	4·5°	CH_3Br
C_2H_6	-84	122	38	C_2H_5Br
C_3H_8	-45	116	71	C_3H_7Br
C_4H_{10}	$+1$	100	101	C_4H_9Br
C_5H_{12}	38	91	129	$C_5H_{11}Br$
C_6H_{14}	71	85	156	$C_6H_{13}Br$
C_7H_{16}	98·4	80·6	179	$C_7H_{16}Br$
C_8H_{18}	125·5	78·5	204	$C_8H_{17}Br$

REPLACEMENT OF HYDROGEN BY NH_2.

Paraffins.	Boiling-point.	Replacement value.	Boiling-point.	*n.* Alkyl amines.
CH_4	$-162°$	156	$-6°$	CH_3NH_2
C_2H_6	-84	102	18	$C_2H_5NH_2$
C_3H_8	-45	94	49	$C_3H_7NH_2$
C_4H_{10}	$+1$	75	76	$C_4H_9NH_2$
C_5H_{12}	38	65	103	$C_5H_{11}NH_2$
C_6H_{14}	71	59	130	$C_6H_{13}NH_2$
C_7H_{16}	98·4	56·6	155	$C_7H_{16}NH_2$
C_8H_{18}	125·5	54·5	180	$C_8H_{17}NH_2$
C_9H_{20}	149·5	45·5	195	$C_9H_{19}NH_2$
$C_{10}H_{22}$	173	45	218	$C_{10}H_{21}NH_2$
$C_{11}H_{24}$	194·5	39·5	234	$C_{11}H_{23}NH_2$
$C_{12}H_{26}$	214	35	249	$C_{12}H_{25}NH_2$
$C_{13}H_{28}$	234	31	265	$C_{13}H_{27}NH_2$

REPLACEMENT OF HYDROGEN BY OH.

Alcohol.	B.P.	B.P. of corresponding paraffin.	Replacement value.
CH_3OH	67°	$-162°$	229
C_2H_5OH	78·3	-84	162·3
C_3H_7OH	97·4	-45	142·4
C_4H_9OH	116·8	$+1$	115·8
$C_5H_{11}OH$	137	38	99
$C_6H_{13}OH$	157	71	86
$C_7H_{16}OH$	175	98·4	76·6
$C_8H_{17}OH$	199	125·5	73·5

Not only does the effect of substitution depend on the number of carbon atoms in the molecule, but also on the number of the substituting groups which have already been inserted. The effect is particularly clear when substitution takes place at one carbon atom. Attention has been drawn to this relation by Henry,[1] Städel,[1] and by Denzel,[1] and some of their results are quoted in illustration.

TABLE XII.

Series.	B.P.	Diff.	Series.	B.P.	Diff.
$C_6H_5CH_3$ . .	111°	65	$CHCl_2COOH$.	194°	1
$C_6H_5CH_2Cl$ . .	176	32	CCl_3COOH .	195	
$C_6H_5CHCl_2$ . .	208	9	$CHCl_2CH_3$ . .	58	56
$C_6H_5CCl_3$ . .	217		$CHCl_2CH_2Cl$.	114	33
CH_3COOH . .	118	67	$CHCl_2CHCl_2$.	147	11
$CH_2ClCOOH$.	185	9	$CHCl_2CCl_3$ . .	158	
$CHCl_2COOH$.	194				

In these cases the effect of the third halogen atom is quite small in comparison with that of the first. It seems to be a general rule that ring formation causes a rise in boiling-point. The cyclo-paraffins are less volatile than the corresponding paraffins; but the difference between the parallel members is not constant.

Cyclo-paraffins.	B.P.	Δ	B.P.	Paraffins.
C_3H_6	−35°	10	−45°	C_2H_6
C_4H_8	+11	10	+1	C_4H_{10}
C_5H_{10}	49	11	38	C_5H_{12}
C_6H_{12}	81	10	71	C_6H_{14}
C_7H_{14}	117	18·6	98·4	C_7H_{16}
C_8H_{16}	148	22·5	125·5	C_8H_{18}
C_9H_{18}	171	21	149·5	C_9H_{20}

When it is considered that the effect of substitution varies according to the number of carbon atoms in the molecule,

[1] Compare references to Table X.

the number of like substituents already present and the symmetry of the product formed, it becomes evident that no comprehensive rule governing substitution can be laid down.

Besides the substitutions mentioned in Table X. many others of a more complex nature have been studied; but these seem rather to be curiosities than to serve any scientific purpose; though it must be remembered that they were discovered in the early days of the subject, when additive properties were more eagerly sought for than at the present time. Some of them are worthy of mention. Berthelot[1] found that when two organic compounds form a new compound with loss of water, the boiling-point of the product is equal to the sum of those of the two components less about 100–120.° Thus—

	B.P.			B.P.
Acetic acid	118°	*n*. Hexylic acid		205°
n. Propyl alcohol . . .	97·4	Ethyl alcohol		78·3
Sum =	215·4		Sum =	283·3
n. Propyl acetate =	101·0	Ethyl *n*. hexylate	=	167·0
	114·4			116·3

	B.P.
Propyl alcohol	97·4°
Methyl alcohol	67·0
Sum =	164·4
Methyl propyl ether =	37·0
	127·4

Gräbe[2] showed that when two phenyl groups are changed to the phenylene groups of a cyclic compound, the boiling-point is raised about forty degrees.

Schröder[3] has drawn attention to the curious fact that the boiling-points of the methyl ketones, methyl esters and

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[1] *Ann. Chim. Phys.*, [3] **48**, 323 (1856); see also Persoz, *Compt. Rend.*, **60**, 1126 (1865); Mendelejeff, *Jahresbericht über die Fortschritte der Chemie*, **29**, 1858; Flavitzky, *Ber.*, **20**, 1948 (1887); Cohn, *J. Pr. Chem.*, **50**, 38 (1894).

[2] *Ber.*, **7**, 1629 (1874).

[3] *Ber.*, **16**, 1312 (1883); also Cohn, *J. Pr. Chem.*, **50**, 38 (1894).

TABLE XIII.

Phenyl derivative.	B.P.	Diff.	B.P.	Phenylene derivative.
C_6H_5 $\quad$>NH . . C_6H_5	310°	41	354°	C_6H_4 $\mid \quad$>NH C_6H_4
C_6H_5 $\quad$>O . . C_6H_5	252	36	287-8	C_6H_4 $\mid \quad$>O C_6H_4
C_7H_5 $\quad$>S .. . C_6H_5	292·5	41	333	C_6H_4 $\mid \quad$>S C_6H_4
C_6H_5 $\quad$>CH$_2$ . . C_6H_5	261-262	42	304	C_6H_5 $\mid \quad$>CH$_2$ C_6H_4

corresponding acid chlorides are often almost identical. Thus—

$C_2H_5COCH_3$ . . 79·5–81° $C_6H_5COCH_3$ . . 199–200°

$C_2H_5COOCH_3$ . . 79·9 $C_6H_5COOCH_3$ . . 199·2

C_2H_5COCl . . . 79·5 C_6H_5COCl . . . 198·7

§ 6. *APPLICATIONS OF BOILING-POINT RELATIONS*

The application of boiling-point to chemical problems is very limited ; but Vernon[1] has shown how the property may be employed to prove association[2] in a compound. If the boiling-point of a liquid is abnormally high, it may be inferred that association has taken place. Thus, on passing through the series of the halogen acids

$$\text{HI} \qquad \text{HBr} \qquad \text{HCl} \qquad \text{HF}$$
$$- 34° \qquad - 73° \qquad - 80° \qquad + 19·4$$

we find that the boiling-point falls in the first three members. By extrapolation the boiling-point of hydrofluoric acid should

[1] *Chem. News*, **64**, 54 (1891).

[2] The influence of association has been discussed also by Henry, *Bull. Acad. Belg.*, 842 (1907).

lie at any rate below $-80°$, whereas it is found to be $+19\cdot4$. Hence this acid would be associated.[1] In the mercaptans sub-traction of CH_2 from the composition lowers the boiling-point, the difference between methyl mercaptan and the last term —sulphuretted hydrogen—being as much as seventy degrees. In the hydroxyl compounds the position of water is entirely abnormal, and hence it follows that this substance is asso-ciated—

C_2H_5OH . .	$78°$	C_2H_5SH .	$+36°$
CH_3OH . . .	$67°$	CH_3SH .	$+ 6°$
H_2O	$100°$	H_2S . .	$-64°$

That the alcohols as a class are inclined to association is shown by the fact that the rise in boiling-point usually pro-duced [2] by exchange of oxygen for sulphur, becomes a fall on passing from an alcohol to a mercaptan. The following list illustrates the relation :—

TABLE XIV.

Substance.	Boiling-point.	Substance.	Boiling-point.
CH_3OCH_3. . .	$-23°$	CH_3SCH_3 . .	$37\cdot5°$
$CH_3OC_2H_5$ . .	$+11$	$CH_3SC_2H_5$ . .	67
$C_2H_5OC_2H_5$ . .	35	$C_2H_5SC_2H_5$ . .	91
n. C_3H_7OH . . .	$97\cdot4$	n. C_3H_7SH . . .	68
C_2H_5OH . . .	78	C_2H_5SH . . .	36
CH_3OH . . .	67	CH_3SH . . .	$+6$

These conclusions are confirmed in general outline by other methods.

Longuinescu[3] has recently discovered a relation between the boiling-point of a liquid and the number of atoms in the molecule.   He finds that with any pair of unassociated liquids, the respective absolute boiling-points (T and T'), the densities

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[1] See Thorpe and Hambly, *Trans. Chem. Soc.*, **55**, 163 (1889).

[2] See also Earp, *Phil. Mag.*, [5] **35**, 458 (1893).

[3] *Journ. de Chim. et de Phys.*, 1, 288, 296, 391 (1903) ; **6**, 552 (1908).

at zero centigrade (D and D′), and numbers of atoms in the molecules (n and n') are related as follows :—

$$\frac{T}{T'} = \frac{D}{D'}\sqrt{\frac{n}{n'}}$$

or $$\frac{T}{D\sqrt{n}} = \frac{T'}{D'\sqrt{n'}} = \text{const. (K)} = 100 \text{ (approx.)}$$

With associated liquids the relation does not hold, and the value of K is always above 100. Assuming the normal value of K for monomolecular liquids to be 100, we may employ the relation in the form—

$$\left(\frac{T}{100 \times D}\right)^2 = n$$

to calculate the number of atoms in a molecule, and thence form an estimate of the degree of association. A few data chosen from the large number collected by Longuinescu to support these conclusions is given in the table. The centre columns in the lists show the number of atoms in the molecules calculated by this process, and the right-hand columns show the number required by theory for the compound in the monomolecular state.

TABLE XV.

Substance.	n. (calc.)	n. (theory)	Substance.	n. (calc.)	n. (theory)
Methylene dichloride	5	5	Ethyl cinnamate .	26	25
Acetyl chloride . .	8	7	Methyl diphenyl		
Furfurane . . .	12	11	amine	28	27
Chlorobenzene . .	12	12	Menthone . . .	28	29
Ethyl propionate .	16	17	Decane	33	32
			Octyl ether . . .	49	51
Hydrofluoric acid .	9	2	Water	14	3
Carbon disulphide .	6	3	Hydrogen sulphide .	5	3
Silicon tetrachloride .	5	5	Phosphoryl chloride	5	5
Hydrocyanic acid .	18	3	Tetrachloroethane .	6	6
Ammonia. . . .	14	4	Sulphur dioxide. .	3	3

§ 7. *THE INFLUENCE OF PRESSURE*

The question whether Kopp's quantitative laws hold at all pressures has been much discussed,[1] but it remained in an unsatisfactory state until Ramsay and Young[2] published their exhaustive researches on the vapour pressures of liquids. If a substance, A, has the absolute boiling-points T_A and T_A' at two different pressures, P and P', and a substance, B, the absolute boiling-points T_B and T_B' at the same pressures, then—

$$\frac{T_{A'}}{T_{B'}} = \frac{T_A}{T_B} + c(T_{B^2}' - T_B)$$

The constant c is usually quite small, and with many substances—for example, the esters of the fatty acids—it is zero. In these cases the relation may be written, as—

$$\frac{T_A'}{T_B'} = \frac{T_A}{T_B} \quad \text{or} \quad \frac{T_A' - T_A}{T_B' - T_B} = \frac{T_A}{T_B} = q$$

whence it is seen that the ratio of the change in the boiling-points of two liquids for a given pressure difference is the same. The qualitative relations which we have observed between the boiling-points of homologues and of isomers will hold at all pressures of comparison; but only, be it remembered, with compounds which give $c = o$ in the foregoing relation.

The so-called "laws" connecting boiling-point and constitution are not of a fundamental character; indeed, it would be surprising if they were, since they are founded on comparisons of the arbitrary temperatures at which the vapour pressures of the liquids overcome that of the atmosphere.

[1] Landolt, *Zeit. für Chem.*, 359, 1868; Winkelmann, *Wied. Ann.*, 1, 430 (1877); Schumann, *Wied. Ann.*, 12, 40 (1881); Schmidt, *Zeit. Phys. Chem.*, 7, 466 (1891); 8, 628 (1891); Kahlbaum, *Studien über Dampf-spannkraftmessungen* (1893); *Ber.*, 27, 3366 (1894); 28, 1675 (1895); Dühring, *Wied. Ann.*, 11, 163 (1880); 51, 223 (1894); 52, 536 (1894); Mangold, *Wien. Ber.*, 102, 1095 (1863).

[2] *Phil. Mag.*, [5] 20, 515; 21, 23, 135; 22, 32 (1887); also Young, *Phil. Mag.*, [5] 34, 510 (1892).

Nernst[1] suggested that the comparison of the vapour pressure curves would give better results than the temperatures corresponding to atmospheric pressure, and the question was more closely studied by Bingham,[2] who found that the constants for the curves of different substances may be additively calculated from values assigned to the component atoms.

With regard to the general character of these boiling-point relations, we may say that they are constitutive; additive relations can be detected, but they are subject to the influence of constitution. It should be observed that Walden[3] has recently shown that the absolute boiling temperature of a liquid is proportional to its specific cohesion.

§ 8. *LATENT HEAT OF VAPORIZATION*

Instead of comparing the temperatures at which the vapour pressures of liquids equal that of the atmosphere, it would seem more profitable to compare their heats of vaporization. The heat of vaporization of a liquid may be defined as the amount of heat required to convert one gram at T degrees under the pressure p into vapour at the same temperature and pressure. If this quantity be denoted by L, then the molecular heat of vaporization, or the heat required to convert one gram molecule of liquid into vapour under the same conditions, will be ML.

When a liquid is vaporized, a portion of the heat absorbed is consumed in doing internal work against molecular cohesion, whilst a further quantity is expended on external work. The latter amount may be expressed as—

$$\frac{P(V - V_L)}{J}$$

where P = the external pressure,

     V and V_L = the volumes of vapour and liquid respectively,

and J = the mechanical equivalent of heat.

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[1] *Theoretische Chemie*, p. 315 (1898).

[2] *Journ. Amer. Chem. Soc.*, **28**, 717 (1906).

[3] See p. 29.

We may then write the total heat of vaporization L as—

$$L = L_m + \frac{P(V - V_L)}{J}$$

where L_m is the true heat of vaporization.

The value of $P\frac{(V - V_L)}{J}$ is in any case fairly small, and for different substances will be almost identical.

Trouton[1] has discovered a fundamental relation between the molecular heat of vaporization and the boiling-point. According to Trouton's law the absolute boiling temperature is proportional to the molecular heat of vaporization measured at that temperature. The law is not strictly true, since the ratio—

$$\frac{ML}{T} \qquad (T = \text{absolute boiling temperature})$$

varies somewhat in different classes of compounds. In most substances it lies very near to 21, but it is especially large with associated bodies like the alcohols, which give $\frac{ML}{T}$ equal to about 26. Nevertheless the law holds very closely for substances of a similar chemical nature. It is therefore to be •
expected that in comparing the molecular heats of vaporization we shall meet with relations similar to those which are found with boiling-point.

The following lists of isomerides and homologues have been collected from various sources, but the comparisons are made with data from the same observer.

From these numbers it may be inferred that isomeric substances of similar structure and chemical nature have approximately the same molecular heats of vaporization. It seems also that chain-branching lowers the heat of vaporization. In the two homologous series quoted the difference for CH_2 is fairly constant, with the exception of the interval between ethyl and propyl alcohols.

[1] *Phil. Mag.*, [4] 54 (1884).

TABLE XVI.

ISOMERIC ESTERS.

Substance.	$\dfrac{ML}{100}$	Substance.	$\dfrac{ML}{100}$
Ethyl formate . . .[2]	68·2	Propyl acetate . .[1]	84·8
Methyl acetate . . .	69·5	Ethyl propionate . .	83·4
Propyl formate. . .[1]	79·3	Methyl butyrate . .	81·3
Ethyl acetate . . .	77·5	Ethyl butyrate . .[2]	82 9
Methyl propionate. .	78·5	Propyl propionate .	82·9
Ethyl isobutyrate . .[2]	80·2	Methyl isobutyrate .[2]	77·3
Isobutyl acetate . .	81·0	Isobutyl formate . .	78·5

ISOMERIC ALCOHOLS.

n. Propyl alcohol . .[3]	99·8	n. Butyl alcohol . .[3]	106
Isopropyl alcohol . .	96·6	Isobutyl alcohol . .	102·4
Octyl alcohol . . .[3]	126·6	Sec. butyl alcohol .	100·8
Sec. octyl alcohol . .	123·5	Tert. butyl alcohol .	96·5

ISOMERIC ESTERS.[3]

Methyl isovalerate	83·9	Ethyl isovalerate . .	88·1
Ethyl isobutyrate . .	83·4	Propyl butyrate . .	88·8
Ethyl butyrate . . .	85·3	Isoamyl acetate . .	89·7
Propyl propionate . .	85·5	Isobutyl isobutyrate .	91·3
Butyl acetate . . .	85·7	Isobutyl butyrate . .	93·0
Isobutyl acetate . .	83·9	Isoamyl propionate .	94·0
Isoamyl formate . .	85·5		

HOMOLOGUES.

Substance.	$\dfrac{ML}{100}$	Diffce. for CH_2.
Methyl alcohol [3]	83·8	
Ethyl alcohol	89·5	5 7
n. Propyl alcohol	99·8	10·3
n. Butyl alcohol	105·9	6·1
n. Heptyl alcohol	121·8	5·3×3
n. Octyl alcohol	126·6	4·8
Ethyl formate [2]	68·2	
Ethyl acetate	73·1	4·9
Ethyl propionate	78·6	5·5
Ethyl butyrate	82·9	4·3
Ethyl valerate	84·1	1·2

[1] Marshall and Ramsay, *Phil. Mag.*, [5] 41, 38 (1896).

[2] Schiff, *Ann.*, 234, 338 (1886).

[3] Brown, *Trans. Chem. Soc.*, 83, 987 (1903).

The following list is given to illustrate the effect of replacing hydrogen by chlorine ; as with boiling-point, the effect falls off with increasing number of halogen atoms :—

Substance.	$\dfrac{ML}{100}$	Difference.
Methyl chloride [1]	48·6	
Methylene chloride [2]	64	15·4
Chloroform [3]	70	6
Carbon tetrachloride [3]	71	1

Very much more research is required before it can be claimed that these relations are of a general nature.

[1] Berthelot and Ogier, *Comptes Rendus*, **92**, 771 (1881).

[2] Chappuis, *Ann. Chim. Phys.*, [6] 19, 517 (1888)⌡

[3] Marshall, *Phil. Mag.*, [5] **43**, 27 (1897).

OPTICAL PROPERTIES

CHAPTER VIII

REFRACTIVE POWER

I. The Physical Nature of Refractivity

§ 1. *REFRACTIVE INDEX*

THE velocity with which ether vibrations of a given period are propagated varies according to the medium which they traverse. Light travels fastest in vacuo, but in space partially occupied by matter the velocity is diminished. Thus when light passes from a vacuum into an isotropic medium the speed of propagation is changed on entering the latter, and the ray is bent out of its course or refracted at the surface. It may be shown by the application of Huyghens' principle that the relation between the sines of the angles of incidence and refraction is constant, and is equal to the ratio of the velocities of light in the two media. Thus, if i is the angle of incidence, and r the angle of refraction, and v^1 and v^2 the velocities of light in the two consecutive media, we have—

$$\frac{\sin i}{\sin r} = \frac{v^1}{v^2} = n$$

This ratio is usually denoted by n and, in the case which we have considered where light passes from vacuum into the substance, it is called the absolute refractive index. When light passes from one substance to another, n expresses the refractive index relatively to the first, and in practice this is usually air.

In the following pages we shall examine the refractive

power of different substances, and endeavour to determine the
influence of chemical constitution on this property; but before
doing this we must consider how the experimental data may
be brought into a form suitable for comparison.

The velocity of light in space containing matter depends
on the wave length of the vibration, and hence with any given
angle of incidence, rays of different wave length will be refracted
to a different extent. If a composite ray undergoes refraction
in a medium it is broken up into homogeneous rays of different
wave length; this is known as dispersion. The connection
between dispersive power and chemical constitution also will
be considered.

It is clear that in order to obtain comparable values the
refractive indices of substances must be measured with
light of some standard wave length. It is usual to employ
light corresponding to the A or D lines in the sun spectrum
or the a and γ lines of the hydrogen spectrum; the latter are
now more frequently chosen. Where the refractive index for
a given wave length has not been measured by experiment it
may be calculated with the aid of Cauchy's formula—

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \text{etc.}$$

which expresses the relation between wave length (λ) and
refractive index (n) for substances whose dispersion is normal.
A represents the refractive index for waves of infinite length.
In practice the shortened form

$$n = A + \frac{B}{\lambda^2}$$

is sometimes used. The refractive index for the required
wave length may then be interpolated from measurements made
with two other values of λ. Opinion seems divided as to
the reliance which may be placed on the result. Most observers
agree that the process is quite trustworthy if the two extreme
values of λ lie close together. Over wide ranges of the
spectrum or for extrapolation to obtain the value of A the

formula cannot be relied upon;[1] whilst for substances where the dispersion is anomalous it entirely fails.[2]

The refractive index also varies considerably with the physical state of the substance, and here the density is by far the most important factor. Several formulæ have been proposed to connect the refractive index of a substance with the density, and of these the earliest

$$\frac{n^2 - 1}{d} = R' = \text{constant}$$

was based on the emission theory of light, from which it was derived by Laplace.[3] Although this formula did not agree very well with experimental data,[4] it remained in use for many years, and even when the emission theory had given place to the undulatory theory attempts were made to reconcile it to the latter.[5] A final effort to justify the use of this formula was made in 1861 by Schrauf,[6] who proposed to replace n by A, the index of refraction for waves of infinite length derived from Cauchy's formula; but this was of no avail, and it was discarded in favour of a simpler expression which had been empirically established by Gladstone and Dale[7] in 1858. This takes the form

$$\frac{n - 1}{d} = R'' = \text{constant}$$

In 1880 a third formula was advanced almost simul-

[1] Gladstone, *Trans. Chem. Soc.*, **45**, 251 (1884); Langley, *Wied Ann.*, **22**, 598 (1884); Bruhl, *Ann.*, **235**, 233 (1886); **236**, 240 (1886); on the other hand, see Eykman, *Chem. Weekblad*, **3**, 657 (1906).

[2] For a better expression of the relations between wave length and refractive index, see Helmholtz, *Pogg. Ann.*, **154**, 582 (1875); *Wied. Ann.*, **48**, 389 (1893); v. Ketteler, *Theoret. Optik.*, 540, *Braunschweig* (1885).

[3] *Mécanique Céleste*, [4] **10**, 237 (1805).

[4] Arago and Petit, *Ann. Chim. Phys.*, **1**, 1 (1816); Gladstone and Dale, *Phil. Trans.*, **155**, 321 (1865).

[5] Hock, *Pogg. Ann.*, **112**, 347 (1861).

[6] *Pogg. Ann.*, **119**, 461 (1863).

[7] *Phil. Trans.*, **148**, 887 (1858).

taneously by Lorentz[1] of Leyden, and Lorenz[2] of Copenhagen—

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} = R''' = \text{constant}$$

The former deduced the expression from Maxwell's electromagnetic theory of light, whilst the latter showed that it may be derived from the undulatory theory with the assumption that the volume of a substance is not completely filled with matter, but that between the spherical molecules there are insterstices in which light travels with the same speed as in a vacuum.   More recently Dufet[3] and Sutherland[4] have obtained theoretical proof of Gladstone's expression.   Other relations[5] have been proposed, and these have each certain advantages; but since they have not been extensively applied to this subject we may confine our attention solely to the Gladstone-Dale and Lorentz-Lorenz formulæ.

The question as to which of these formulæ best expresses the relation between density and refractive index has been much discussed, and both the n and n^2 expressions have been tested in a variety of ways, but as yet no definite conclusion has been reached, for neither is quite accurate.   The majority of the data with which we shall deal have been derived from liquids, and for these either expression is satisfactory.[6]

[1] *Wied. Ann.*, **9**, 641 (1880).

[2] *Wied. Ann.*, **11**, 70 (1880).

[3] *Bull. Soc. Mineral.*, **6**, 261 (1885).

[4] *Phil. Mag.*, **27**, 141 (1889).

[5] Johst, *Wied. Ann.*, **20**, 47 (1883), gives $\frac{\sqrt{n}-1}{d} = \text{const.}$; von Ketteler, *Wied. Ann.*, **33**, 356 (1888); **35**, 662 (1888), recommends $(n^2 - 1)(v - \beta) = c(1 - \alpha c^{-\kappa t})$, where β represents the portion of the specific volume (v) actually filled with matter; Edwards, *Amer. Chem. Journ.*, **16**, 625 (1894); **17**, 473 (1895), gives $\frac{n-1}{nd}$. For others see Zecchini, *Gazz.*, **25**, 269 (1895); Hibbert, *Phil. Mag.*, [5] **40**, 268 (1895); Eykmann, *Rec. Pays. Bas.*, **14**, 185 (1895); **15**, 52 (1896).

[6] Weegmann, *Zeit. Phys. Chem.*, **2**, 257 (1888); Eykmann, *Rec. Pays.*, **12**, 163 (1893); Landolt, *Pogg. Ann.*, **123**, 595 (1864); Rühlman, *Pogg. Ann.*, **132**, 202 (1867); Gladstone and Dale, *Phil. Trans.*, **817** (1863); Perkin, *Trans. Chem. Soc.*, **61**, 309 (1892); Quincke, *Wied. Ann.*, **19**, 401 (1883); Zehnder, *Wied. Ann.*, **34**, 117 (1888).

English chemists have usually employed the Gladstone-Dale formula, whilst German and Italian seem to prefer the Lorenz-Lorentz expression. The temperature correction for either is very small. According to Eykman the molecular refraction measured by the n formula decreases by 0·003 units for a rise in temperature of one degree centigrade; with the n^2 formula the value increases by the same amount. If great accuracy be desired the measurements may be thus reduced to a standard temperature; but generally this has been neglected, since within ordinary limits the temperature correction is within experimental error.

§ 2. *SPECIFIC AND MOLECULAR REFRACTIVE POWER*

The specific refractive power expresses the relation between the refractive index and density of a substance.

$$\left.\begin{array}{l} \dfrac{n-1}{d} = R \\[2ex] \dfrac{n^2-1}{n^2+2} \cdot \dfrac{1}{d} = r \end{array}\right\} \text{specific refractive power}$$

and the products of these and the molecular weight of the substance is called the " molecular refractive power."

$$\left.\begin{array}{l} (n-1)\dfrac{m}{d} = M \\[2ex] \dfrac{n^2-1}{n^2+2} \cdot \dfrac{m}{d} = \mathcal{M} \end{array}\right\} \text{molecular refractive power}$$

It is possible, with certain limitations, to assign to each atom in the molecule a definite share in the total refractive power, and this is called the atomic refractivity. The molecular refractivity may then be represented as the sum of the refractive effects of the component atoms. It has been generally assumed that the refractive effect of a given atom is constant for all substances in which the mode of linkage of the atom is the same; but if the valency or situation of the atom be changed, the refractive effect is modified accordingly. Bearing in mind these limitations of the additive law,

we may write the molecular refractivity of a substance as follows :—

$$M = x'R' + x''R'' + \text{etc.} \quad \text{(Gladstone-Dale)}$$
$$\text{or } \mathfrak{M} = xr + x''r \qquad \text{etc.} \quad \text{(Lorentz-Lorenz)}$$

where x', x'', etc., are the numbers of each kind of atom in a given situation, and R', R'', etc., their respective refractive effects. Since we shall later examine the data from either formula, the different notation employed should be carefully noted.

The specific refractive power of a liquid compound is obtained by the measurement of density and refractive index at the same temperature ; but when the substance to be investigated is a solid, it is usually examined in solution. It is generally assumed that the refractivity of mixtures[1] of non-electrolytes is determined solely by the super-position of the refractivities of the separate components. In these circumstances the specific refractive power of the solute may be calculated from that of the solution by the admixture formula :

$$W\frac{N - 1}{D} = w_1\frac{n_1 - 1}{d_1} + w_2\frac{n_2 - 1}{d_2}$$

where W, N, and D are respectively the weight, refractive index, and density of the mixture, and w_1, n_1, d_1, etc., the corresponding values for each constituent taken separately. The method does not always give satisfactory results, especially in cases where some alteration in volume takes place on mixing the components.   Pulfrich has shown that in these cases a

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[1] The investigations dealing with the refractivity of mixtures are very numerous; the following are the chief references : Landolt, *Pogg. Ann.*, **122**, 545 (1863) ; **123**, 595 (1864) ; Wüllner, *ibid.*, **133**, 1 (1868) ; Johst, *Wied. Ann.*, **28**, 56 (1885) ; Pulfrich, *Zeit. Phys. Chem.*, **4**, 561 (1889) ; Schütt, *ibid.*, **9**, 349 (1892) ; Forch, *Drud. Ann.*, **8**, 675 (1900) ; Kowalski, *Compt. Rend.*, **133**, 33 (1901) ; Rudolphi, *Zeit. Phys. Chem.*, **37**, 426 (1901) ; Berghoff, *Zeit. Phys. Chem.*, **15**, 422 (1894) ; Leduc, *Compt. Rend.*, **134**, 645 (1902) ; Von Aubel, *Arch. de Genève*, [4] **15**, 78 (1903) ; Verschaffelt, *Bull. Soc. Roy. Belg.*, **27**, 3 (1904) ; Homfray, *Trans. Chem. Soc.*, **87**, 1430 (1905).

correction for the change in volume may be applied. How-
ever, generally speaking, the simple admixture formula is
accurate if the solvent and solute have nearly the same
refractive index ; but if these differ much from one another,
confidence cannot be placed in the result.

II. REFRACTIVITIES OF THE ELEMENTS DERIVED FROM INORGANIC SUBSTANCES

§ 3. *BY DIRECT MEASUREMENT OF THE ELEMENTS*

A remarkable relationship between the refractivity of the
gaseous elements and their relative positions in the periodic sys-
tem has been detected by Cuthbertson.[1] In the nitrogen, oxygen,
fluorine and neon families, the refractive power $(n - 1)$ increases
in simple integral ratios on ascending to the elements of higher
atomic weight. Moreover, the ratio of the increase is the same
between corresponding members of each family. So far as
can be judged from the data which are at present available, it
seems that the regularity is not quite exact, and is confined to
a certain portion of the periodic arrangement. The annexed
table illustrates the more salient features of the relationship.

TABLE I.

VALUES OF $(n - 1)10^6$ FOR SOME ELEMENTS, MEASURED IN THE GASEOUS STATE.

				He
—	—	—	—	$144 \times 0\cdot5$
—	N	O	F	Ne
	297	270	192	137
—	P	S	Cl	Ar
	299×4	275×4	192×4	142×4
Zn	As	Se	Br	Kr
243×6	258×6	261×6	187×6	142×6
Cd	Sb	Te	I	Xe
267×10	—	249×10	192×10	138×10

[1] Cuthbertson, *Phil. Trans.*, **204**, 323 (1905) ; *Science Progress*, **10**, 1
(1908) ; Cuthbertson and Prideaux, *Phil. Trans.*, **205**, 319 (1905) ; Cuth-
bertson and Metcalfe, *Phil. Trans.*, **207**, 135 (1907) ; C. and M. Cuth-
bertson, *Proc. Roy. Soc.*, 81 (1909).

In this connection it may be of interest to observe that the refractive indices of some of the metals have been directly measured. Kundt[1] successfully prepared thin wedge-shaped plates whose refracting angle was sometimes as small as 11″. Also, the method of reflection has been employed by Drude[2] in measuring the refractive indices of metals. The results from the two sources are collected in the following table, and it will be seen that they are by no means concordant. The

TABLE II.

KUNDT: *n* MEASURED WITH SODIUM OR WHITE LIGHT.

Metal.	*n*.	Metal.	*n*.
Silver	0·27	Platinum . . .	1·64
Gold	0·58	Iron	1·73
Copper	0·65	Nickel	2·01

DRUDE: *n* MEASURED FOR THE D LINE.

Metal.	*n*.	Metal.	*n*.
Sodium	0·0045	Silver	0·18
Magnesium . . .	0·37	Cadmium . . .	1·13
Aluminium . . .	1·44	Tin	1·48
Iron	2·36	Antimony . . .	3·04
Gold	0·36	Lead	2·01
Nickel	1·79	Copper	0·64
Mercury	1·73	Zinc	2·12

densities of the samples of metals examined were not measured, hence the values of the refractivities cannot be given. The most interesting aspect of these results is that they show the refractive index of some of the metals to be less than unity. According to the refractive index of sodium, light travels some 200 times faster in this metal than in air.

[1] *Wied. Ann.*, **34,** 469 (1888); **36,** 824 (1889).
[2] *Wied. Ann.*, **34,** 523 (1888); **36,** 548 (1889); **39,** 537 (1890); **42,** 189 (1891); **64,** 159 (1898).

§ 4. *REFRACTIVE EQUIVALENTS OBTAINED FROM COMPOUNDS*

(*a*) *Gases.*—If we attempt to reconstruct the molecular refractivity of a gaseous compound by summation of the refractivities of the component elements or gaseous compounds, we find that in most cases the result does not agree very closely with experiment.[1] Some illustrations of this process are quoted in the following table.

TABLE III.

Substance.	M (obs.).	M (calc.) from—	Difference per cent.
Hydrochloric acid	6·70	H+Cl = 6·83	+2
Hydrocyanic acid	6·63	H+CN = 7·21	+8·7
Water	3·82	H_2+O = 4·14	+8·4
Carbonyl chloride	17·32	CO+Cl_2 = 16·59	−4·4
Ammonia	5·63	N+3H = 5·36	−5
Carbon dioxide	6·71	CO+O = 7·08	−5·5
Nitrous oxide	7·58	N_2+O = 6·45	−17·5
Nitric oxide	4·46	N+O = 4·25	−5
	$(n_D-1)10^6.$		
Sulphur hexafluoride	783	S+6F = 1140	+32·0
Selenium hexafluoride	896	Se+6F = 1367	+34·5
Tellurium hexafluoride	991	Te+6F = 1832	+45·0
Phosphoretted hydrogen	786	P+H_3 = 811	+3·8
Phosphorus trichloride	1730	P+3Cl = 1755	+1·4

The percentage divergence between the calculated and experimental values is shown in the right-hand column of the table, and it will be seen that the summation law does not hold. We here have distinct evidence of the constitutive nature of this property. Brühl has shown that the refractive power of gaseous hydrogen, chlorine, and bromine are approximately the same as the atomic refractivities of these elements calculated from organic compounds. But it is very doubtful whether this relation holds with elements of higher

[1] Brühl, *Zeit. Phys. Chem.*, **7**, 1 (1891); Cuthbertson, *Science Progress*, **10**, 17 (1908); Dulong, *Ann. Chim. Phys.*, [2] **31**, 154 (1826).

atomic weight, especially those of varying valency.   Indeed, as will be later demonstrated, the refractive values of such elements are not constant even in organic compounds.

(*b*) *From Crystalline Solids.*—The optical data from solid inorganic salts have been collected from numerous sources by Pope,[1] who employed them to calculate [2] the atomic refractivities of the elements.   The resulting figures show that the refractive effects of the elements in any vertical column of the periodic arrangement, as a rule, increase continuously with rising atomic weight, but no simple numerical relation can be detected.

TABLE IV.

Element.	R_D.	Element.	R_D.
Lithium	4·45	Magnesium . . .	8·81
Sodium	4·1 .	Zinc	12·40
Potassium	7·64	Cadmium . . .	16·53
Rubidium	10·31	Strontium . . .	13·95
Cæsium	15·25	Barium . . .	18·94
Chlorine	10·99	Aluminium . . .	14·61
Bromine	17·26	Gallium	16·52
Iodine	29·04	Lead	30·02

(*c*) *From Aqueous Solutions of Electrolytes.*—The refractive equivalents of a large number of the elements have been deduced from aqueous solutions of salts ; but before examining these data we shall briefly inquire into the influence of the state of dilution on the refractive index of the dissolved salt.[3]

[1] *Trans. Chem. Soc.,* **69**, 1530 (1896) ; replacement values of the elements in crystalline solids have been studied by Tutton, *Trans. Chem. Soc.,* **69**, 344, 507 (1896).

[2] The method employed varies according to the crystalline form of the substance ; see Dufet, *Bull. Soc. Mineral.,* **10**, 77 (1887).

[3] The chief literature on the refractive index of salt solutions is to be found in the following : Beer and Kremers, *Pogg. Ann.,* **101**, 133 (1857) ; Hofmann, *ibid.,* **133**, 155 (1868) ; Le Blanc, *Zeit. Phys. Chem.,* **4**, 553 (1889) ; **19**, 264 (1896) ; Schutt, *ibid.,* **5**, 349 (1890) ; Hallwachs, *Wied. Ann.,* **47**, 380 (1892) ; **50**, 577 (1893) ; **53**, 1 (1894) ; **68**, 1 (1899) ; **55**, 282 (1895) ; Bender, *ibid.,* **38**, 89 (1890) ; **68**, 343 ; **69**, 676 (1899) ; *Drud. Ann.,* **2**, 186 (1900) ; **8**, 109 (1902) ; Gladstone and Hibbert, *Trans. Chem.*

It has been suggested that the refractive index (n) of an aqueous solution of an electrolyte may be represented by an expression of the form—

$$n = n_0 + ap + bp^2 + cp^3$$

where n_0 is the refractive index of the solvent and p is the weight of salt in one hundred parts by weight of water. But there is no doubt that this expression is not quite accurate and that it cannot be applied with equal success to all salts. The exhaustive experiments carried out by Gladstone and Hibbert show that the influence of solution on the salt is very complex. In most cases the molecular refractivity of a solid electrolyte is slightly altered by solution in water. The behaviour of different salts is not uniform ; some increase and others decrease in refractivity on passing into solution, but whatever the nature of the change, it is continued, though in a far smaller degree, on further dilution. The effect of dilution is more pronounced with concentrated solutions ; but with decreasing concentration the molecular refractivity tends to become constant. The phenomena stand in very close relation to those observed with the magnetic rotation of the plane of polarized light ; and it is clear that the usual theory of electrolytic dissociation cannot entirely explain them. Walden's experiments with his normal salt —tetraethyl ammonium iodide—in various organic media, seem to show that the influence of dissociation on refractivity is inappreciable. As, indeed, might be expected, the molecular refraction of the salt varies from solvent to solvent, but there is no relation between the dissociating power of the solvent and the effect on the refractivity of the dissolved salt. Moreover, in moderately dilute solutions the molecular refractive power of this salt is independent of the concentration.

Soc., **67**, 831 (1895) ; **71**, 822 (1897) ; Dijken, *Zeit. Phys. Chem.*, **24**, 81 (1897) ; Zoppellari, *Gazz. Chim. Ital.*, **25**, 269 (1895) ; **35**, 65 (1905) ; Zecchini, *ibid.*, **35**, 355 (1905) ; Bary, *Compt. Rend.*, **114**, 327 (1892) ; **118**, 17 (1894) ; Wallot, *Drud. Ann.*, **11**, 593 (1905) ; Chèneveau, *Ann. Chim. Phys.*, [8] **12**, 145, 289 (1907) ; Walden, *Zeit. Phys. Chem.*, **59**, 385 (1907).

But it must be admitted that in some cases the refractivity of a dissolved electrolyte is clearly influenced by dissociation. For example, Le Blanc and Rohland have found that the molecular refractivities of many organic acids in aqueous solution increase with dilution, and they conclude that hydrogen in the ionic condition has a greater refractive effect than the non-ionised element.

In spite of this uncertainty as to the influence of the dissolved state and dilution on the refractivity of salts, the refractive equivalents of numerous elements have been calculated [1] from the refractivity of salt solutions. By employing solutions of known strength, the molecular refraction of the dissolved salt may be calculated by the usual admixture formula. Then the refractivity of one ion is subtracted from this molecular value, leaving the required atomic refraction of the element. The data obtained by different observers are not concordant, and we shall therefore confine our attention to the observations of Gladstone, which have led to the more interesting results. The specific refractions $\left(\dfrac{n-1}{d}\right)$ and atomic refractions of some elements referred to Frauenhofer's A line in the solar spectrum are shown in the following table. It cannot be claimed that the refractive equivalents are constant, for the value depends on the manner in which the element is combined. The values quoted in the table are deduced from compounds in which the elements play the part of an electro-positive radicle; if in combination with oxygen an element assumes an electro-negative character the value is entirely altered. Further, it should be noticed that the refractive equivalent varies according to the valency displayed by the element. Gladstone has drawn attention to a very interesting relation between the specific refraction of a metal and its equivalent weight. The

[1] Gladstone, *Proc. Roy. Soc.*, 439 (1868); **60**, 140 (1896); Gladstone and Hibbert, *Trans. Chem. Soc.*, **67**, 831 (1895); **71**, 822 (1897); Kannonikow, *J. Pr. Chem.*, [2] **31**, 321 (1885); Le Blanc, *Zeit. Phys. Chem.*, **4**, 553 (1884); **19**, 261 (1896); Hauke, *Wien. Ber.*, **105**, IIA, 749 (1896); Bromer, *Wien. Ber.*, **110**, IIA, 929 (1901); Dinkhauser, *Wien. Ber.*, **114**, IIA, 1001 (1905).

product of the specific refraction and the square root of the equivalent is constant—

$$SE^{\frac{1}{2}} = \text{constant}$$

With univalent metals this is approximately 1·30, but with bivalent, tervalent, quadrivalent, and quinquevalent elements

TABLE V.

Element.	Specific refraction.	Atomic refraction.	Element.	Specific refraction.	Atomic refraction.
Hydrogen .	1·488	1·5	Arsenic .	0·200	15·0
Lithium .	0·514	3·6	Selenium .	0·339	26·8
Beryllium .	0·733	6·7	Bromine .	0·190 etc.	15·2
Boron . .	0·436–0·317	4·8 etc.	Rubidium .	0·133	11·4
Carbon .	0·383	4·6	Strontium .	0·152	13·3
Nitrogen .	0·343 etc.	4·8 etc.	Yttrium	0·197	17·6
Oxygen .	0·203 etc.	3·25 etc.	Zirconium .	0·242	21·9
Fluorine .	0·031	0·6?	Rhodium .	0·232	23·9
Sodium .	0·202	4·66	Palladium .	0·213	22·7
Magnesium	0·287	6·99	Silver . .	0·121	13·1
Aluminium	0·352	9·5	Cadmium	0·124	13·9
Silicon .	0·250 etc.	7·1 etc.	Iridium .	0·153	17·4
Phosphorus	0·594	18·4 etc.	Tin . .	0·232 etc.	27·6 etc.
Sulphur .	0·422 etc.	13·5 etc.	Antimony	0·204 etc.	24·5 etc.
Chlorine .	0·282 etc.	10·0 etc.	Iodine .	0·192 etc.	24·4 etc.
Potassium	0·205	8·0	Cæsium .	0·117	15·6
Calcium .	0·252	10·1	Barium .	0·117	16·1
Titanium .	0·522	25·1	Lanthanum	0·143	19·9
Vanadium .	0·481	24·6	Cerium .	0·143	20·1
Chromium	0·296	15·4	Iridium .	0·165	31·9
Manganese	0·208	11·5	Platinum .	0·172	33·5
Iron . .	0·209 etc.	11·7 etc.	Gold . .	0·127	25·1
Nickel .	0·186	10·9	Mercury .	0·107 etc.	21·5 etc.
Cobalt .	0·183	10·8	Thallium .	0·106	21·6
Copper .	0·184	11·7	Lead . .	0·129 etc.	26·7 etc.
Zinc . .	0·151	9·9	Bismuth .	0·154	32·0
Gallium .	0·214	15·0	Thorium .	0·123	28·7

it is the same throughout, being about 1·01. This clearly shows that a connection exists between the valency and refractivity of an atom; and we have found further evidence of this in dealing with the relations between valency and volume.

Hauke has studied the relation between the refractive power of the elements and their positions in the periodic table.

He finds that the atomic refractivity increases to a maximum at the middle of each period and then falls off towards the end. Further, the refractivity of the elements in a given "family" increases with rising atomic weight.

III. Refractivity and Chemical Structure of Organic Compounds

§ 5. *HISTORICAL*

The refractivity of organic substances has been closely studied for the past fifty years, and the relations between this and chemical structure are perhaps better known than with any other property. Refractivity is both additive and constitutive, but as in other cases the efforts of the earlier investigators were focussed on the additive aspects of the property. The first experiments on this subject were conducted in 1805-6 by Biot and Arago,[1] who claimed to have shown that the refractivity of gaseous compounds is equal to the sum of the refractivities of the constituents in the gaseous state. According to this conclusion, refractivity would be a purely additive property; but the gases which Biot and Arago investigated had refractive indices very close to unity, and unless very accurate experimental methods had been used the results could scarcely be regarded as conclusive. Indeed, Dulong[2] some twenty years later published a series of very accurate measurements which showed that the statement made by Biot and Arago was not true; mixtures of gases were found to obey the additive law, but when combination took place the product had sometimes a greater and sometimes a smaller refractivity than the sum of the effects of the constituents. Isomeric substances were first studied by Deville[3] and by Becquerel and Cahours,[4] who found that liquid isomeric esters of the same density

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[1] *Mém. de l'Instit. de France,* **7**, 301 (1806); *Gilb. Ann.,* **25**, 345; **26**, 36 (1807).

[2] *Ann. Chim. Phys.,* [2] **31**, 154 (1826).

[3] *Compt. Rend.,* **11**, 865 (1840); *Pogg. Ann.,* **51**, 433 (1840).

[4] *Compt. Rend.,* **11**, 867 (1840); *Pogg. Ann.,* **51**, 427 (1840).

had the same refractive index. A decade later Delffs[1] and Berthelot[2] examined a few homologous series. The work of the latter is especially noteworthy, since it was the first attempt to give a quantitative expression of the refractivity of a group. Berthelot found that the molecular refractivity increases in ascending homologous series, and from the few data at his disposal he calculated that the increase in refractivity caused by the addition of a methylene group is equal to about 18 units (Laplace's formula).

These researches prepared the way for the classical work of Gladstone and Dale[3] and of Landolt,[4] who may be said to have laid the foundation of the subject. In 1863 Gladstone and Dale published the data obtained from a number of isomeric substances; the results showed that these have the same refractivity only if their chemical nature is the same. In the words of the original memoir, it was concluded that "every liquid has a specific refractive energy composed of the specific refractive energies of the component elements modified by the manner of combination." It is interesting to notice that this statement, which is the first definite mention of the constitutive nature of the property, still holds good after nearly fifty years of subsequent research. Gladstone and Dale also found that the refractivity of homologues rises with increasing molecular weight, and thus confirmed the observations of Delffs and Berthelot. Landolt's results were published[5] in the following year. His measurements were perhaps more accurate than those previously made, and he was able to show that the molecular refractivity of isomeric fatty acids and esters is the same. With homologues he found that the specific refractivity increases with additional CH_2, but the effect falls off somewhat on ascending the series; the molecular refractivity increases by an approximately constant amount for each methylene group added and the average value of the increase, calculated from the Gladstone-Dale

[1] *Pogg. Ann.*, **81**, 470 (1850).
[2] *Ann. Chim. Phys.*, [3] **48**, 342 (1856).
[3] *Phil. Trans.*, **153**, 217 (1863).
[4] *Pogg. Ann.*, **123**, 595 (1864).
[5] *Pogg. Ann.*, **122**, 535 ; **123**, 595 (1864).

formula, was found to be about 7·6. Landolt employed this value to calculate from the empirical formulæ of a series of substances the atomic refractivities of carbon, hydrogen, and oxygen; but the values he obtained were vitiated by constitutive influences which he did not at the time recognize.

Attention was now turned to the influence of constitution, and in 1870 Gladstone[1] showed that the molecular refractivity of an unsaturated compound is greater than that calculated from Landolt's values for the elements. Brühl commenced his investigations about 1880. He was the first to calculate[2] the refractivity of an element under different structural conditions, and he was able to obtain independent values for hydroxylic and carbonyl oxygen; and later,[3] at the suggestion of Conrady's[4] observations, Brühl found another value for oxygen in ethers and esters. From this stage the subject advanced very rapidly More material was available, new classes of compounds were examined, and the optical constants of several elements were obtained. The modern development of the relations between refractivity and structure, especially the refractive power of nitrogen and of tautomeric compounds, and the application of the data to problems of constitution in organic chemistry, are due chiefly to Brühl.

We shall now in detail examine the more important relations between refractivity and structure.

§ 6. GENERAL CHARACTER OF REFRACTIVE POWER

Choosing at random several pairs of isomeric substances, and comparing their refractive power, we find that in many instances the molecular refractivity is quite different. A closer examination of the material shows that isomers of a similar chemical nature and structure have almost the same molecular refractive power, the difference in many cases being within

[1] *Trans. Chem. Soc.*, **23**, 147 (1870).

[2] *Ann.*, **203**, 1 (1880); *Ber.*, **13**, 1119 (1880); *Zeit. Phys. Chem.*, **7**, 167 (1891).

[3] *Zeit. Phys. Chem.*, **7**, 172 (1891).

[4] *Zeit. Phys. Chem.*, **3**, 210 (1889).

experimental error. On the other hand, where the disparity is great the isomers have a widely different structure. For illustration of this behaviour the annexed list may be consulted; the data are drawn from several different sources.

TABLE VI.

Substance.	$\mathfrak{M}\alpha$.	Substance.	$\mathfrak{M}\alpha$.
Amyl valerate . . .	49·69	Isoamyl nitrite . . .	31·44
Amyl isovalerate . . .	50·05	Aniline	30·27
Propyl isovalerate . .	40·80	Methyl pyridine . .	28·66
Isopropyl isovalerate. .	40·90	Nitrooctane	44·58
Butyl isovalerate . . .	45·31	Nitrodiisobutyl . . .	44·78
Isobutyl isovalerate . .	45·30	Benzyl cyanide . . .	34·94
Sec. butyl isovalerate .	45·48	*o.* Tolyl nitrile . . .	36·06
Butyl caproate . . .	54·49	Phenyl hydrazine . .	33·71
Isobutyl caproate . .	54·36	Dimethyl pyrazine . .	31·93
Sec. butyl caproate . .	54·10	Menthol	47·52
Ethylene chloride . .	20·95	Allyl dipropyl carbinol .	48·85
Ethylidene chloride . .	21·08	Terpineol.	46·95
Ethylene bromide . .	26·84	Diallyl propyl carbinol .	48·27
Ethylidene bromide . .	27·31	Aldehyde	11·50
Angelic acid	26·95	Paraldehyde	3 × 10·80
Tiglic acid	26·96	Ar. tetrahydro β naph-	
Methyl citraconate . .	37·84	thylamine	45·88
Methyl itaconate . . .	38·03	Ac. tetrahydro β naph-	
Acrolein	16·01	thylamine	46·66
Propargyl alcohol . .	14·83	Propyl aldehyde . . .	15·93
Diethyl allyl carbinol .	39·72	Allyl alcohol . . .	16·85
Methyl hexyl ketone . .	39·07	Propionic acid . . .	28·57 [1]
Allyl ethyl ether . .	26·39	Methyl acetate . . .	29·36 [1]
Valeric aldehyde . . .	25·31	Ethyl formate . . .	29·18 [1]
Isobutyl mercaptan . .	28·32	Caproic acid	51·61 [1]
Diethyl sulphide . . .	28·14	Methyl valerate . . .	51·71 [1]
Nitropropane	21·30	Ethyl butyrate . . .	51·32 [1]
Propyl nitrite	22·10	Amyl formate . . .	52·09 [1]
Nitroisopentane . . .	30·57		

We have here sufficient evidence to show the additive and constitutive nature of refractivity; indeed, it was from similar evidence that Gladstone and Dale acutely deduced the true character of the property. The additive nature of refractivity was referred to by these investigators, but it was first clearly

[1] These values refer to Mα (Gladstone-Dale); see Landolt, *Pogg. Ann.*, **123**, 595 (1864).

demonstrated by Landolt. It has already been mentioned that from consideration of homologous series of the fatty acids, alcohols, and esters he obtained the value of 7·6 for CH_2. A few of the data in support of this may be mentioned.

TABLE VII.

Substance.	Ma.	Δ	Substance.	Ma.	Δ
Acetic acid . .	21·11		Methyl acetate .	24·36	6·81
Propionic acid .	28·57	7·46	Ethyl acetate .	31·17	
Butyric acid . .	36·22	7·65	Methyl butyrate .	43·97	7·35
Valeric acid . .	44·05	7·83	Ethyl butyrate .	51·32	
Caproic acid . .	51·61	7·56	Methyl valerate .	51·71	7·49
Oenanthylic acid .	59·40	7·79	Ethyl valerate .	59·20	

Subtracting the value of nCH_2 from the molecular refractivities of the acids $C_nH_{2n}O_2$, a fairly constant residue for O_2 is obtained. The mean of these values was 6, whence $O = 3$. From the refractive power of the alcohols $C_nH_{2n+2}O$ the values of nCH_2 and O were taken, leaving the refractive effect of $H_2 = 2·6$. Hence $H = 1·30$. Again, subtracting 2·6 (H_2) from the effect of CH_2 (7·6), the value of carbon was found, $C = 5$. Landolt tested these values by calculating with them the molecular refractivity of a substance from its empirical formula. Thus in the case of propyl alcohol C_3H_8O the molecular refractivity would be $3 \times 5 + 8 \times 1·3 + 3 = 28·4$. Observation gave the value 28·3. Inserting the calculated molecular refractivity for M in the equation

$$\frac{(n-1)m}{d} = M \quad \text{or} \quad n = 1 + \frac{M}{m} \cdot d$$

the refractive index was obtained, and generally the agreement with the observed number was very good, as may be seen from the following examples (Table VIII.).

Landolt therefore concluded that the molecular refractivity of a compound is equal to the sum of the constant effects of the atoms which form the compound. Further confirmation of this rule was obtained by showing that mixtures containing the

same proportion of carbon, hydrogen, and oxygen had the same refractivity.

TABLE VIII.

Substance	n_a observed.	n_a calculated.
Acetic acid	1·370	1·371
Propionic acid	1·385	1·388
Methyl acetate	1·359	1·352
Ethyl acetate	1·371	1·373
Aldehyde	1·330	1·326
Acetone	1·357	1·353
Ethyl alcohol	1·361	1·362
Propyl alcohol	1·379	1·381

Later work, especially that of Gladstone and Brühl, has brought out the constitutive nature of refractivity. It is now known that the refractive power of an atom is not constant, but varies according to the valency and manner of linkage of the atom and the nature of the groups with which it is united. We have already had indication of this in some of the comparisons of isomeric substances. With simple substances it is possible to assign a definite refractive value to a particular modification of structure ; but before approaching this question the effect of CH_2 in homologous series must be examined, since the value of this group is taken as the basis for calculating all the others.

§ 7. *HOMOLOGOUS SERIES*

On surveying the optical data from a homologous series it is evident that the specific refractive power increases with molecular weight ; but the increase for every additional CH_2 is not constant, since it falls off on ascending the series. On the other hand, the increase in *molecular* refractivity appears constant, though here, also, there probably is a small decrease in the effect of CH_2 on passing up the series ; but it is quite within experimental error. The data for the fatty alcohols [1] are given in the table.

[1] Brühl, *Zeit. Phys. Chem.*, **7**, 159 (1891).

TABLE IX.

Substance.	$r_{a}.$	Δ	$\mathfrak{M}_{a}.$	Δ	
Methyl alcohol	0·2550		8·16		CH_4O
Ethyl alcohol	0·2762	0·0212	12·71	4·55	C_2H_6O
Propyl alcohol	0·2903	0·0141	17·42	4·71	C_3H_8O
Butyl alcohol	0·2974	0·0071	22·01	4·59	$C_4H_{10}O$
Isobutyl alcohol	0·2967		21·96		$C_4H_{10}O$
Isoamyl alcohol	0·3025	0·0058	26·62	4·66	$C_5H_{12}O$
Isopropyl alcohol	0·2907		17·44		C_3H_8O
Trimethyl carbinol	0·2985	0·0078	22·09	4·65	$C_4H_{10}O$
Methyl hexyl carbinol	0·3104	(0·0040)5	40·35	(4·58)5	$C_8H_{18}O$
		Mean . . .		+4·616	

The average value for the refractive effect of CH_2 has been calculated from homologous series by several chemists. As we have seen in a foregoing paragraph, Berthelot was the first to attempt this; but his data are too few to give confidence in the result. Landolt's values are more trustworthy. He obtained[1] from the fatty acids, alcohols, and acids the numbers—

$$CH_2, \ R_a = 7·60, \ and \ r_a = 4·56$$

The values of Brühl[2] are now usually accepted, since they were obtained from a larger range of material—in all about 150 substances. In each homologous series the value for CH_2 was found by subtracting the first from the last, the first but one from the last but one, and so on, and then multiplying each of these differences by the number of CH_2 groups in the interval between the pairs of substances. The sum of the resulting numbers was then divided by the total number of CH_2 groups represented. Thus with the alkyl iodides we have—

$$\mathfrak{M}_a$$

Methyl iodide, CH_3I . . . . . 19·25
Ethyl iodide, C_2H_5I . . . . . 24·09
Propyl iodide, C_3H_7I . . . . . 28·73
Butyl iodide, C_4H_9I . . . . . 33·25

[1] Landolt, *Pogg. Ann.*, **123**, 611 (1864) ; *Ann.*, **213**, 75 (1882).
[2] Brühl, *Zeit. Phys. Chem.*, **7**, 140 (1891).

Difference between		CH_2 groups in interval.	Product.	CH_2 groups represented in product.
1st and 4th	14·00	3	42·00	9
2nd and 3rd	4·64	1	4·64	1
			46·64	10

The total difference for an interval of ten CH_2 groups is thus 46·64, whence the average for one CH_2 is 4·664. Other series were similarly dealt with, and the mean value for each was found to be approximately constant.

	Intervals.	Difference.	Average.
Alcohols	17	78·48	4·616
Aldehydes . . .	29	131·72	4·542
Ketones	5	23·02	4·60
Acids.	48	219·20	4·566
Ethers	10	45·82	4·582
Esters	60	272·46	4·541
Oxychlorides . .	5	22·56	4·512
Bromides . . .	9	42·09	4·677
Iodides	10	46·64	4·664
	193	881·99	4·570

Thus the average refractive value of —CH_2— for the a hydrogen line is $r_a = 4\cdot570$ in the Lorenz-Lorentz formula. Also Conrady[1] has calculated the refractive power of this group for the sodium D line. In obtaining the average he employed the more laborious method of least squares, and the result was

$$r_D = 4\cdot60 = CH_2$$

There is no doubt that the effect of CH_2 depends to a certain extent on the nature of the compound in which it

[1] *Zeit. Phys. Chem.*, **3**, 210 (1889).

occurs.   The experiments of Eykman[1] and of Landolt[2] have shown that the lower members of a series are usually irregular, and this may be ascribed to the fact that the methylene group, being then alone or attached to only one carbon atom, has a different situation from that occupied in the higher members, where it is attached to two other carbon atoms. Conrady, however, recognized this in calculating the value of carbon.   The irregularity referred to is illustrated below with the fatty acids.

TABLE X.

Substance.		M_a.	Δ	$\mathfrak{M}_a$.	Δ
Formic acid . .	CH_2O_2	13·91		8·52	
Acetic acid . .	$C_2H_4O_2$	21·11	7·20	12·93	4·41
Propionic acid .	$C_3H_6O_2$	28·71	7·60	17·42	4·49
Butyric acid . .	$C_4H_8O_2$	36·50	7·79	22·05	4·63
Isovalerianic acid	$C_5H_{10}O_2$	44·05	7·55	26·72	4·67
Isocaproic acid .	$C_6H_{12}O_2$	51·61	7·56	31·22	4·50
Heptylic acid .	$C_7H_{14}O_2$	59·40	7·79	35·85	4·63
Nonylic acid . .	$C_9H_{18}O_2$	75·19	2(7·89)	45·13	2(4·64)
Lauric acid . .	$C_{12}H_{24}O_2$	98·29	3(7·70)	59·27	3(4·71)
Palmitic acid. .	$C_{16}H_{32}O_2$	129·19	4(7·71)	77·68	4(4·60)
Stearic acid . .	$C_{18}H_{36}O_2$	144·64	2(7·72)	86·92	2(4·62)
Cerotic acid . .	$C_{27}H_{54}O_2$	214·03	9(7·71)	128·34	9(4·60)

It is worthy of notice that this behaviour is shown with other physical properties, such as magnetic rotation, melting-point, and boiling-point.

Eykman has also pointed out that the value of the methylene group slightly varies in different classes of compounds; indeed, this is evident from Brühl's results.   Perhaps the best illustration is given by the esters of oxalic and malonic acids, where the value of CH_2 varies according to whether it is inserted in the acid or alcoholic radicle.

[1] *Rec. Pays. Bas.*, **12**, 160, 248 (1893) ; **13**, 13 (1894) ; **14**, 185 (1895) ; **15**, 32 (1896).
[2] *Pogg. Ann.*, **123**, 595 (1864).

TABLE XI.

Substance.	M_a.	Δ	Substance.	M_a.	Δ
Methyl malonate .	47·14	2(7·68)	Methyl oxalate .	39·76	7·38
Ethyl malonate .	62·51		Methyl malonate	47·14	
Methyl oxalate .	39·76	2(7·73)	Ethyl oxalate .	55·22	7·29
Ethyl oxalate . .	55·22		Ethyl malonate .	62·51	

Nevertheless the effect of constitution on the refractive power of CH_2 is usually very small and lies within the limits of experimental error, so that for practical purposes the values of Landolt, Brühl, and Conrady may be used as a basis of calculation. It may be here mentioned that Eykman finds the average for CH_2 measured for the *a* hydrogen line with the Gladstone-Dale formula [1]

$$R_a = 7·587$$

a number quite in accordance with that of Landolt. When determined [2] from hydrocarbons, where disturbing influences are reduced to a minimum, it was

$$R_a = 7·772 \qquad r_a = 4·613$$

§ 8. *CARBON, HYDROGEN, AND OXYGEN*

As previously explained, the older values for these elements had been calculated by Landolt [3] from the value of CH_2 with the assumption that oxygen had a constant effect in all classes of compounds. ·Brühl,[4] however, found that the oxygen in aldehydes has a different value from the hydroxylic oxygen of acids. The effect of *doubly bound oxygen* (O″) was obtained by subtracting from the molecular refraction of the aldehydes ($C_nH_{2n}O″$) the effect of nCH_2; thus, taking R_a (Gladstone) = 7·6, and r_a (Lorentz) = 4·57 for CH_2, we have the following :—

[1] See also Perkin, *Trans. Chem. Soc.*, **77**, 267 (1900).
[2] *Chem. Weekblad*, **3**, 657 (1906).
[3] *Pogg. Ann.*, **123**, 595 (1864).
[4] Brühl, *Ann.*, **203**, 1 (1880).

TABLE XII.

Substance.	Subtracted.	M_a.	$R_a(O'')$.	$\mathfrak{R}_a$.	$r_a(O'')$.[1]
Acetaldehyde . . .	$2CH_2$	18·61	3·41	11·50	2·36
Propionic aldehyde .	$3CH_2$	26·00	3·20	15·93	2·22
Acetone	$3CH_2$	26·16	3·36	16·05	2·34
Butyraldehyde. . .	$4CH_2$	33·68	3·28	20·52	2·24
Isobutyl aldehyde .	$4CH_2$	33·64	3·24	20·56	2·28
Isovaleraldehyde . .	$5CH_2$	41·60	3·60	25·31	2·46
Oenanthol	$7CH_2$	56·82	3·62	34·20	2·21
Methyl hexyl ketone .	$8CH_2$	—	—	39·07	2·51
		Mean .	3·4		2·328

Whence $R_a(O'') = 3·4$ and $r_a(O'') = 2·328$.

The value of *hydroxylic oxygen* (O') was obtained from the molecular refraction of the fatty acids $(C_nH_{2n}O''O')$ diminished by either the molecular refraction of the corresponding aldehyde $(C_nH_{2n}O'')$, or by the calculated value of $n(CH_2)O''$. In the following table the former plan is illustrated together with another similar method.

TABLE XIII.

Substance.	M_a.	$R_a O'$.	$\mathfrak{R}_a$.	$r_a O'$.
Acetic acid . . .	21·15	2·54	12·93	1·43
Acetaldehyde. . .	18·61		11·50	
Propionic acid . .	28·62	2·62	17·42	1·49
Propionaldehyde. .	26·00		15·93	
Butyric acid . . .	36·33	2·65	22·05	1·53
Butyraldehyde . .	33·68		20·52	
Isobutyric acid . .			22·03	1·47
Isobutyraldehyde .			20·56	
Isovalerianic acid .	44·12	2·52	26·72	1·41
Isovaleraldehyde. .	41·60		25·31	
Oenanthylic acid .	59·50	2·68	35·85	1·65
Oenanthol . . .	56·82		34·20	
Glycol			14·33	1·62
Ethyl alcohol . .			12·71	
Lactic acid . . .	31·87	3·25	19·09	1·67
Propionic acid . .	28·62		17·42	
Glycerine			20·41	$2 \times 1·50$
Propyl alcohol . .			17·42	
	Mean .	2·80 appxt.		1·518

[1] Brühl, *Zeit. Phys. Chem.*, **7**, 166 (1891).

The mean of all values for $r_a O''$ was found to be 1·506.

The effect of *ethereal oxygen* ($O <$) was found by subtracting from the molecular refraction of the fatty esters $C_n H_{2n} O'' O <$ the calculated value of $n(CH_2)O''$; the mean of all the values, which was obtained in the manner already described, was 1·665 = $r_a O <$. By combining these values of oxygen with that of the methylene group the refractive *equivalent* of *hydrogen* was calculated in several different ways. Some of these are illustrated below.

<center>TABLE XIV.</center>

Substance.	Formula.	Subtracted value.		$\mathfrak{M}_a$.	$\Delta = r_a H_2$.
Ethyl alcohol . . .	$C_2 H_6 O'$	$2CH_2 O'$	10·65	12·71	2·06
Methyl hexyl carbinol	$C_8 H_{18} O$	$8CH_2 O'$	38·07	40·35	2·28
Glycol	$C_2 H_6 O'_2$	$2CH_2 O'_2$	12·15	14·33	2·18
Glycerine	$C_3 H_8 O'_3$	$3CH_2 O'_3$	18·23	20·41	2·18
Ethyl ether . . .	$C_4 H_{10} O <$	$4CH_2 O <$	19·94	22·31	2·37
Methylal	$C_3 H_8 O_2 <$	$3CH_2 O_2 <$	17·02	19·10	2·08
Hexane	$C_6 H_{14}$	$6CH_2$	27·42	29·70	2·28

Thus the mean value of $r_a H_2$ was shown to be 2·205, whence $r_a H = 1·103$, and for carbon ($r_a CH_2 = 4·57$) $r_a C = 2·365$. Conrady[1] recalculated r_a for the D sodium line and found—

$$r_D O' = 1·521 \qquad r_D H = 1·051$$
$$r_D O'' = 2·287 \qquad r_D C^\circ = 2·592$$
$$r_D O < = 1·683 \qquad r_D C' = 2·501$$

Here the values for C° and C' refer to carbon alone, as in methyl alcohol, and to carbon united to one or two other carbon atoms.

Miss Homfray,[2] from a study of the refractive power of salts and other derivatives of γ pyrone, finds the refractive value of *quadrivalent oxygen* $r_a O^{IV}$ to be about 2·7.

Eykman[3] has recently determined the refractivity of

[1] *Zeit. Phys. Chem.*, **3**, 210 (1889).
[2] *Trans. Chem. Soc.*, **87**, 1443 (1905).
[3] *Chem. Weekblad*, **3**, 656 (1906).

hydrogen in a manner similar to that pursued by Brühl. By subtracting the molecular refractive power of n octane from that of dotriacontane ($C_{32}H_{66}$), and dividing the result by twenty-four, the value of CH_2 was found to be —

$$R_aCH_2 = 7\cdot7717 \text{ and } \mathfrak{R}_aCH_2 = 4\cdot6132$$

Eight times the value for CH_2 was then taken from the molecular refractive power of n octane (C_8H_{18}); the residue gave the refractive equivalent of the terminal hydrogen atoms.

$$R_aH_2 = 2\cdot144 \quad \text{and} \quad r_aH_2 = 2\cdot120$$
$$R_aH = 1\cdot072 \quad \text{and} \quad r_aH = 1\cdot060$$

§ 9. *UNSATURATED CARBON*

In 1870 Gladstone,[1] while investigating aromatic compounds, observed that the molecular refractivities of these substances were always higher than the values calculated for them from their empirical formulæ with the aid of Landolt's data. He stated that this was probably connected with their richness in carbon in comparison with aliphatic derivatives. The anomaly was subsequently explained by Brühl,[2] who found that the increase in refractive power is due to the presence of unsaturated carbon. From comparisons made with aliphatic and aromatic compounds he showed that the discrepancy between the calculated and experimental values increases in proportion to the number of ethenoid linkages. When one double bond is present the difference is

$$M_a \text{ (obs.)} - M_a \text{ (calc.)} = 2\cdot4$$

with two

$$M_a \text{ (obs.)} - M_a \text{ (calc.)} = 4\cdot5$$

and from aromatic compounds in which three ethenoid bonds were assumed

$$M_a \text{ (obs.)} - M_a \text{ (calc.)} = 7\cdot2$$

[1] *Trans. Chem. Soc.*, **23**, 147 (1870).
[2] *Ann.*, **200**, 139 (1879).

Hence the effect of the double bond was taken to be approximately $R_a I = = 2·4.$[1]

At a later date, when more material had been collected, Brühl[2] and Conrady[3] recalculated the value from the Lorenz-Lorentz formula. Some of the data employed by Brühl are quoted in the table.

TABLE XV.

Substance.	$\mathfrak{M}_a$ (obs.).	$\mathfrak{M}_a$ (calc.).	Difference.
Allyl alcohol . . .	16·85	15·22	1·63
Amylene	24·64	22·86	1·78
Acrolein	16·01	13·84	2·17
Ethyl crotonate . . .	31·49	29·21	2·28
Octylene	38·61	36·57	2·04
Allyl dimethyl carbinol	30·84	28·93	1·91
Allyl diethyl carbinol .	39·72	38·07	1·65
Allyl dipropyl carbinol.	48·85	47·22	1·63
Allyl ethyl ether . .	26·39	24·51	1·88
Valerylene	24·16	20·65	2×1·76
Diallyl	28·77	25·22	2×1·78
Diallyl carbinol . . .	34·88	31·30	2×1·79
Diallyl methyl carbinol.	39·29	35·87	2×1·71
Diallyl propyl carbinol .	48·27	45·01	2×1·63 .
Benzene	25·93	20·81	3×1·73
Chlorobenzene . . .	30·90	25·72	3×1·75
Bromobenzene . . .	33·76	28·57	3×1·76
Toluene	30·79	25·38	3×1·83
Benzyl alcohol . . .	32·23	26·89	3×1·80

The average was calculated from these data, and it was found that $r_a I = = 1·836.$

Quite recently Eykman[4] has very thoroughly investigated the value of the ethenoid linkage, and he finds that it is by no means constant in all classes of compounds, for it varies with the number of carbon chains attached to the ethylenic carbon atoms. The effect of unsaturation was estimated by comparing

[1] See also Kannonikow, *Ber.*, **14**, 1697 (1881); and Landolt, *Ann.*, **213**, 78 (1882).

[2] *Zeit. Phys. Chem.*, **7**, 179 (1891); **1**, 307 (1887).

[3] *Zeit. Phys. Chem.*, **3**, 210 (1889).

[4] Eykman, *Chem. Weekblad*, **3**, 706 (1906).

the unsaturated compounds with the corresponding saturated derivative. Thus—

No side chains.[1]

$$\text{Ethane, } CH_3—CH_3 \quad \mathfrak{M}_a = 11\cdot35$$
$$\text{Ethylene, } CH_2=CH_2 \quad \mathfrak{M}_a = 10\cdot74$$
$$\text{unsaturation} = -0\cdot61$$

One side chain.

$$\text{Hexane, } C_6H_{14} \quad \mathfrak{M}_a = 29\cdot80$$
$$\text{Diallyl, } CH_2=CH—CH_2—CH_2—CH=CH_2 \quad \mathfrak{M}_a = 28\cdot79$$
$$\text{unsaturation} = -1\cdot01 \times 0\cdot5 = -0\cdot50$$
$$n \text{ Valerianic acid, } CH_3CH_2CH_2CH_2COOH \quad \mathfrak{M}_a = 26\cdot72$$
$$\Delta^2 \text{ Pentenic acid, } CH_2=CH—CH_2—CH_2COOH \quad \mathfrak{M}_a = 26\cdot19$$
$$\text{unsaturation} = -0\cdot53$$
$$\text{average value} = -0\cdot52$$

Two side chains.

$$\text{Hexane, } C_6H_{14} \quad \mathfrak{M}_a = 29\cdot80$$
$$\text{Hexylene, } CH_3CH=CH(CH_2)_2CH_3 \quad \mathfrak{M}_a = 29\cdot44$$
$$\text{unsaturation} = -0\cdot36$$
$$\text{Octane, } C_8H_{18} \quad \mathfrak{M}_a = 39\cdot03$$
$$\text{Octylene, } CH_3CH=CH(CH_2)_4CH_3 \quad \mathfrak{M}_a = 38\cdot64$$
$$\text{unsaturation} = -0\cdot39$$
$$\text{average value} = -0\cdot37$$

Three side chains.

$$\text{Methyl hexylketone, } CH_3COC_6H_{13} \quad \mathfrak{M}_a = 39\cdot08$$
$$\text{Methyl heptenone, } CH_3COCH_2CH_2CH=C(CH_3)_2 \quad \mathfrak{M}_a = 38\cdot84$$
$$\text{unsaturation} = -0\cdot24$$

Collecting these values and adding to them the refractive effect of $2H$, we may obtain the corresponding values of the ethenoid linkage.

---

[1] Eykman finds the average decrease in the value of unsaturation to be $0\cdot14$ for each successive substitution. Hence by extrapolation he obtains the value for the unsaturation without side chains as $0\cdot66$.

TABLE XVI.

Effect of unsaturation + value of $2H$ = ethenoid linkage

Unsubstituted	. . $- 0\cdot 61 + 2\cdot 12 =$	$1\cdot 51$	$\mathbf{1}^{=(0)}$
Singly substituted	. $- 0\cdot 52 + 2\cdot 12 =$	$1\cdot 60$	$\mathbf{1}^{=(1)}$
Doubly substituted	. $- 0\cdot 37 + 2\cdot 12 =$	$1\cdot 75$	$\mathbf{1}^{=(2)}$
Trebly substituted	. $- 0\cdot 24 + 2\cdot 12 =$	$1\cdot 88$	$\mathbf{1}^{=(3)}$
Quadruply substituted	$- 0\cdot 1 + 2\cdot 12 = circ.\ 2\cdot 0$		$\mathbf{1}^{=(4)}$

The value of the quadruply substituted ethenoid linkage is obtained by extrapolation. It will be later shown how Eykman has employed these values for unsaturation to determine the position of a double bond in a chain of carbon atoms.

Also the effect of *the acetylene bond*[1] has been determined, but the data are very few, and the result is therefore somewhat doubtful.

TABLE XVII.

Substance.	$\mathfrak{M}_\alpha$ (obs.).	$\mathfrak{M}_\alpha$ (calc.).	Δ.
Propargyl alcohol	$14\cdot 83$	$13\cdot 01$	$1\cdot 82$
Propargyl ethyl ether . . .	$24\cdot 54$	$22\cdot 30$	$2\cdot 24$
Propargyl acetate	$24\cdot 57$	$22\cdot 43$	$2\cdot 14$
Heptidene	$32\cdot 46$	$29\cdot 79$	$2\cdot 67$

The average obtained from these data is $r_\alpha\mathrm{I}{\equiv} = 2\cdot 22$. More recently Moureu[2] has examined a number of substances prepared in the course of his investigation of acetylene derivatives. He observed that the presence of acidic or unsaturated groups has a considerable effect on the value of the acetylene bond, and he therefore proposes to employ as the normal the value deduced from hydrocarbons. With the data from amyl and hexyl acetylene Moureu found this normal value to be about $2\cdot 49$.

[1] Brühl, *Ann.*, **200**, 139 (1879); **235**, 82 (1886); *Zeit. Phys. Chem.*, 1, 6 (1887); **7**, 2, 191 (1891).
[2] *Ann. Chim. Phys.*, [8] 7, 536 (1906).

NORMAL VALUE TO BE ABOUT 2·49.

	$\mathfrak{M}_\alpha$ (obs.).	$\mathfrak{M}_\alpha$ (obs.) $-\mathfrak{M}_\alpha$ (calc.) $=r_\alpha I\!\!\equiv.$
n Amyl acetylene $CH_3(CH_2)_4C\!\equiv\!CH$ . .	32·289	2·498
n Hexyl acetylene $CH_3(CH_2)_5C\!\equiv\!CH$ . .	36·838	2·476

Mean value of $rI\!\!\equiv = 2\cdot487$.

It may be here noted that when an unsaturated group is attached to an ethylenic or acetylenic carbon atom the refractive power of the substance is abnormally high.

§ 10. *THE FORMATION OF SIMPLE RING-SYSTEMS*

The influence of ring-formation on refractivity was first studied by Brühl. From measurements of the refractivities of 'dichloro-trimethylene,[1] paraldehyde,[2] and epichlorohydrine,[3] it was inferred that ring-formation does not influence refractive power; but the data are few, and, in the case of the trimethylene derivative, the discrepancy between the experimental and calculated values seems too large to warrant the conclusion. The data are quoted in the following list :—

	$\mathfrak{M}_\alpha$ (obs.).	$\mathfrak{M}_\alpha$ (calc.).	Δ
Dichlorotrimethylene $CCl_2\!\!<\!\!\begin{array}{c}CH_2\\ \mid\\ CH_2\end{array}$ . .	24·05	23·54	0·51
Paraldehyde	32·40	32·10	0·30
Epichlorohydrine . . .	20·47	20·28	0·19

The experiments of Eykman[4] with derivatives of piperidine and pyrrolidine are more convincing.

[1] Brühl, *Ber.*, **12**, 2146 (1879).
[2] Brühl, *Ann.*, **203**, 43 (1880).
[3] Brühl, *Ber.*, **24**, 657 (1891).
[4] *Ber.*, **25**, 3071 (1892).

TABLE XVIII.

		𝕸ₐ (obs.).	𝕸ₐ (calc.).[1]
Piperidine	CH₂⟨CH₂—CH₂ / CH₂—CH₂⟩NH	26·57	26·56
N. methyl piperidine .	CH₂⟨CH₂—CH₂ / CH₂—CH₂⟩NCH₃	31·66	31·45
N. methyl α pipecoline	CH₂⟨CH₂—CH(CH₃) / CH₂—CH₂⟩N . CH₃	36·07	36·16
N. methyl α methyl pyrrolidine	CH₂—CH(CH₃) / CH₂—CH₂ ⟩N . CH₃	31·59	31·45
N. methyl αα' dimethyl pyrrolidine	CH₂—CH(CH₃) / CH₂—CH(CH₃) ⟩NCH₃	36·07	36·16
αα' Dimethyl pyrrolidine	CH₂—HC(CH₃) / CH₂—HC(CH₃) ⟩NH	31·34	31·13

It is only recently that sufficient data have become available to study the effect of ring - formation in homocyclic systems. Wallach[2] and Willstätter[3] have collected the data from cyclic ketones and hydrocarbons. These are quoted in Table XIX.

The calculated values were obtained from the sum of the refractivities of the component elements, and since the difference between this and the experimental value is in most cases less than 0·10 unit, it is evident that the formation of these cyclic systems has no influence on refractivity. Cyclononane seems to be slightly irregular, but there is some doubt[4] as to the purity of the substance examined. It will be noticed that trimethylene

[1] Obtained from Brühl's values for C, H and N.
[2] Wallach, *Ann.*, **353**, 331 (1907).
[3] Willstätter, *Ber.*, **40**, 3982 (1907); **41**, 1480 (1908).
[4] Willstätter and Kametaka, *Ber.*, **40**, 4876 (1907).

TABLE XIX.

Substance.	*t.*	$\mathfrak{M}_\alpha$ (obs.).	$\mathfrak{M}_\alpha$ (calc.).	Δ
Cyclobutane . .	0°	18·22	18·41	−0·19
Cyclopentane . .	16·0	23·09	23·01	+0·08
Cyclohexane . .	19·5	27·67	27·62	+0·05
Cycloheptane . .	20	32·18	32·22	−0·04
Cyclooctane . .	20	36·58	36·82	−0·24
Cyclononane . .	16	42·36	41·61	+0·75
Cyclopentanone .	—	23·19	23·20	−0·01
Cyclohexanone .	—	27·82	27·80	+0·02
Cycloheptanone .	—	32·32	32·40	−0·08
Cyclooctanone . .	—	36·64	37·00	−·0·36

is not included in this table; but the refractivity of the parent hydrocarbon has not been measured. Tschugaeff,[1] however, has made the interesting observation that the refractivity of trimethylene derivatives[2] is usually greater than the value calculated from the sum of the elements. Thus the optical character of the trimethylene ring is similar to that of the ethylene bond, and it is well known that there is a strong chemical resemblance between the two, notably in their additive capacity and behaviour towards oxidising agents. The data are collected from the observations of Brühl,[3] Tschugaeff,[4] and Zelinsky and Zelikow.[5]

TABLE XX.

Substance.	$\mathfrak{M}_D$ (obs.).	$\mathfrak{M}_D$ (calc.).	Δ
Trimethylene carboxylic acid . .	20·68	20·12	+0·66
1.1 dimethyl trimethylene . .	23·74	23·02	+0·72
1.1.2 trimethyl trimethylene . .	28·81	27·63	+1·18
1.2.3 trimethyl trimethylene . .	28·87	27·63	+1·24
Dichloro trimethylene	24·18	23·70	+0·48

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[1] *Ber.*, **33**, 2122 (1900).

[2] The measurements recently made by Prileschajeff, *Ber.*, **42**, 4811 (1909), seem to show that the formation of ·the ethylene oxide ring is accompanied by a slight increment in refractive power.

[3] *Ber.*, **25**, 1954 (1892); **32**, 1228 (1899).

[4] *Ber.*, **33**, 3122 (1900).

[5] *Ber.*, **34**, 2859, 2867 (1901).

It is evident that the increment for the trimethylene ring varies from about 0·5 to 1·2 units, but it never reaches the value of the ethylenic bond (1·7 for the D line). In carone, a substance of the formula—

$$CH_3 \quad CH_3$$

$$\diagdown \diagup$$

$$C$$

$$\mid$$

$$CH$$

$$CH_2 \qquad CH$$

$$\mid$$

$$CH_2 \qquad CO$$

$$\diagdown CH \diagup$$

$$\mid$$

$$CH_3$$
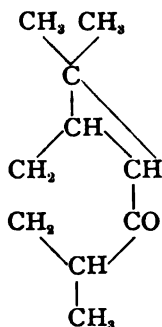
$$\mathfrak{M}_D \text{ (obs.)} = \quad 45\cdot26$$
$$\mathfrak{M}_D \text{ (cal.)} = \quad 44\cdot11$$
$$\Delta = +\ 1\cdot15$$

we find a further resemblance between the optical behaviour of the trimethylene ring and ethenoid linkage. The increment for ring-formation in this compound is about 1·15 units, whilst for the similarly constituted substance thujone it is considerably less.
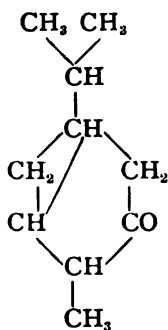
$$CH_3 \quad CH_3 \qquad\qquad CH_3 \quad CH_3$$
$$\diagdown \diagup \qquad\qquad\qquad \diagdown \diagup$$
$$CH \qquad\qquad\qquad\qquad CH$$
$$\mid \qquad\qquad\qquad\qquad\quad \mid$$
$$CH \qquad\qquad\qquad\qquad C$$
$$CH_2 \diagup \quad \diagdown CH_2 \qquad CH_2 \diagup \quad \diagdown CH_2$$
$$\mid \qquad\qquad \mid \qquad\qquad \mid \qquad\qquad \mid$$
$$CH \qquad\qquad CO \qquad CH \qquad\qquad CH_2$$
$$\diagdown CH \diagup \qquad\qquad\qquad \diagdown C \diagup$$
$$\mid \qquad\qquad\qquad\qquad \parallel$$
$$CH_3 \qquad\qquad\qquad\quad CH_2$$

Thujone—$\mathfrak{M}_D$ (obs.) = 44·78   Sabinene—$\mathfrak{M}_D$ (obs.) = 44·8
$\mathfrak{M}_D$ (cal.) = 44·81 $\mathfrak{M}_D$ (cal.) = 43·5
$\Delta = +0\cdot67$ $\Delta = +1\cdot3$
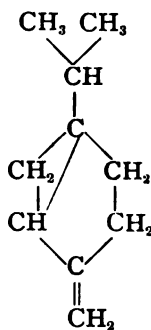
Carone, however, contains the unsaturated carbonyl group adjacent to the trimethylene ring, whereas in thujone these

groups are separated by the saturated methylene group. We shall find in a subsequent chapter dealing with optical anomaly that substances which contain the carbonyl group adjacent to an ethenoid linkage, or any other unsaturated group, show a similar "exaltation." In these cases the carbonyl group is said to be "conjugated" with the ethenoid or trimethylene systems. Sabinene behaves similarly, and it contains the ethenoid linkage in conjunction with the trimethylene ring.

Turning from the derivatives of trimethylene to substitution products of other polymethylenes, it is surprising to find that the refractivities of the latter do not agree so closely with the calculated values as the parent hydrocarbons. The data employed to illustrate this are taken from various sources.

The cause of the discrepancy at present remains doubtful, but it may be noted that Δ is smaller than with the trimethylene derivatives, and apparently least of all with pentamethylene compounds. It seems possible, therefore, that future research may show that the increment for ring-formation in these compounds corresponds to the "tension" in the cyclic system. The experiments recently performed by Eykman add further support to this view. The value of an exocyclic methylene group in the alkyl derivatives of pentamethylene is normal.

Hydrocampholene	.	41·44	Hydroisolaurolene	.	.	36·78
Cyclopentane	. . .	23·01	Cyclopentane	. . .		23·01
$4CH_2 =$		18·43	$3CH_2 =$			13·77
$CH_2 =$		4·61	$CH_2 =$			4·59

But in cyclohexane compounds it is somewhat higher—

Methyl cyclohexane	$= 32·33$	Dimethylcyclohexane	$= 37·04$
Cyclohexane	. . $= 27·54$	Cyclohexane	. . $= 27·54$
$CH_2 =$	4·79	$CH_2 = 9·50/2 =$	4·75

Nasini and Carrara[1] have observed that the refractive power of some heterocyclic compounds, containing unsaturated carbon and other elements, is often lower than the calculated value ;

[1] *Zeit. Phys. Chem.*, **17**, 539 (1895).

but this seems due[1] to the mutual action of the unsaturated groups, and not to ring-formation.

TABLE XXI.

Substance.	Formula.	$\mathfrak{M}_a$ (obs.).	$\mathfrak{M}_a$ (calc.).	Δ
'etramethylene carboxylic acid[2] . .	C_4H_7COOH	25·01	24·48	+ 0·53
lydroisolaurolene[3] .	$CH_2\!-\!CH\!\!\diagdown\!\!\overset{\displaystyle CH_3}{\underset{\displaystyle C(CH_3)_2}{}}$ $CH_2\!-\!CH_2$	36·78	36·56	+ 0·22
lydrocampholene[4] .	$\overset{\displaystyle CH_3\ \ CH_3}{\underset{CH_2-CH_2}{CH-CH}}\diagdown C(CH_3)_2$	41·44	41·14	+ 0·30
lenthane[4] . . .	$CH_3\!-\!CH\!\!\diagup^{CH_2-CH_2}\!\!\diagdown_{CH_2-CH_2}\!\!\diagup CH-CH(CH_3)_2$	46·15	45·71	+ 0·44
3 dimethyl cyclohexane[4] . . .	$CH_3 . CH\!\!\diagup^{CH_2-CHCH_3}\!\!\diagdown_{CH_2-CH_2}\!\!\diagdown CH_2$	37·04	36·56	+ 0·48
1 dimethyl cyclohexane[5] . . .	$(CH_3)_2C\!\!\diagup^{CH_2-CH_2}\!\!\diagdown_{CH_2-CH_2}\!\!\diagup CH_2$	36·80	36·56	+ 0·24
ethyl cyclohexane[4]	$CH_3\!-\!CH\!\!\diagup^{CH_2-CH_2}\!\!\diagdown_{CH_2-CH_2}\!\!\diagdown CH_2$	32·33	32·0	+ 0·33

[1] See *Optical Anomaly*, pp. 284-303.
[2] Brühl, *Ber.*, **32**, 1222 (1899).
[3] Crossley and Renouf, *Trans. Chem. Soc.*, **89**, 1 (1906); Eykman, *Chem. Weekblad*, **4**, 50 (1907).
[4] Eykman, *Chem. Weekblad*, **3**, 690 (1906).
[5] Perkin, *Trans. Chem. Soc.*, **91**, 835 (1907).

§ 11. *FORMATION OF COMPLEX ALICYCLIC SYSTEMS*

Semmler[1] has remarked that many substances containing polycyclic systems exhibit an anomaly similar to that observed with trimethylene derivatives. In support of this, some examples of bi- and tricyclic compounds are given in the appended list.

TABLE XXII.

Substance.	Structure.	$\mathfrak{R}$ (obs.).	$\mathfrak{R}$ (calc.).	Δ
Thujone[4]		(D) 44·78	44·11	+0·67
Pinene[2]		(a) 43·72	43·13	+0·59
Camphene[2]		(a) 43·69	43·13	+0·56
Camphor[3]		M(a) 74·43	74·2	+0·23
Bicyclononane[2]		(a) 39·26	39·03	+0·23
Tricyclodecane		(a) 41·65	41·30	+0·35
Cyclene[2]		(a) 42·46	41·30	+1·16

In obtaining the theoretical values of the unsaturated substances, allowance has been made for the unsaturated group.

[1] *Ber.*, **40**, 1120 (1907).

[2] Eykman, *Chem. Centralblatt.*, II., 1205 (1907).

[3] Kannonikow, *Journ. Prakt. Chem.*, [2] **32**, 504 (1885).

[4] From *Die Aetherische Oele* (Semmler), vols. ii. and iii., Leipzig, 1906–7.

On surveying the table it is evident that the value of Δ is greatest for substances containing the trimethylene ring; but it is important to notice that even here it does not come near the value of the ethylenic linkage. This fact, as we shall find later, has been used in obtaining evidence for the constitution of some of the terpenes.

§ 12. *THE REFRACTIVITIES OF VARIOUS ELEMENTS DEDUCED FROM ORGANIC COMPOUNDS*

In considering the refractivities of carbon and oxygen we have already found sufficient evidence to show that the refractivity of an element varies according to the degree of saturation and the elements with which it is combined. Many other elements have been examined and this conclusion is fully confirmed. Generally speaking, univalent elements, especially those which tend to preserve this valency, do not vary much in refractivity. Hydrogen is a typical case; fluorine, chlorine, and bromine are further examples. On the other hand, multivalent elements, such as nitrogen or sulphur, which display a variety of valency, and pass readily from the lower to the higher degree of saturation, vary considerably in refractive effect. Indeed, for such elements it is not often possible to calculate an average atomic effect with any approach to accuracy, as may be done with carbon and oxygen. Brühl has calculated the atomic refractivities of nitrogen and Nasini those of sulphur, but the values can only be applied to the particular class of compound from which they have been deduced. The illustrations given in the tables further show that the refractivities of these elements vary according to the elements with which they are united, so that the values furnished by inorganic substances often differ widely from those in carbon compounds.

In the following lists the molecular refractivities of substances containing various elements are given. The atomic refractivities were calculated from these in the usual manner, employing the standard values for carbon, hydrogen, and oxygen. The first values to be obtained in this way were

those of chlorine and bromine, and since these were found to be approximately constant, they have since been employed with the previously established refractivities of carbon, hydrogen, and oxygen to obtain the values for the remaining elements. The method when applied to complicated substances is of very doubtful value, since, as we have seen, the standard elements vary under different conditions. The errors which may thus arise are thrown upon the element whose refractivity is sought. Brühl's values for nitrogen are the most reliable, since they have been separately calculated from each class of substance.

TABLE XXIII.

FLUORINE.[1]

Substance.	n_D.	$\mathfrak{M}_D$.	r_D.
CBr_3—CHBrF . . .	1·59707	42·109	0·997
CH_2F—COOCH$_3$ . .	1·36987	17·828	1·130
CCl_3Fl	1·3856	21·598	1·249
CHClBrF	1·42209	19·256	0·95
CBrF=CBrF . . .	1·45345	25·923	0·37
CHF=CBr$_2$ . . .	1·49533	25·855	0·66
C_6H_5F	1·46773	25·926	0·68

CHLORINE.[2]

Substance.	$\mathfrak{M}_\alpha$.	r_α.	Substance.	$\mathfrak{M}_\alpha$.	r_α.
CCl_4	26·40	4×6·01	$CH_2ClCOOC_2H_5$	26·79	5·62
$CHCl_3$ . . .	21·31	3×5·95	$CHCl_2COOC_2H_5$	32·03	2×5·99
CH_2Cl—CH_2Cl.	20·92	2×5·89	$CCl_3COOC_2H_5$.	37·08	3×6·04
CH_3—$CHCl_2$.	21·08	2×5·97	C_2H_5COCl . .	25·66	6·15
CH_3COCl . .	16·74	6·37	CCl_3CHO . .	26·37	3×6·07
$CH_3CH_2CH_2Cl$.	20·75	5·93	$C_2H_4ClCOOC_2H_5$	36·39	6·08

$$r_\alpha = 6·014$$

[1] Swarts, *Chem. Cent.*, II., 1042 (1897). Swarts claims that fluorine varies in refractive effect according to whether the substance is saturated or not. In the former circumstance the average for $r_D = 1·082$, in the latter $r_D = 0·775$. In any case it is worth noticing that fluorine has a very small refractivity, nearly equal to that of hydrogen, and the atomic volume is correspondingly small.

BROMINE.[2]

Substance.	$\mathfrak{M}_a.$	$r_a.$	Substance.	$\mathfrak{M}_a.$	$r_a.$
C_2H_5Br . . .	18·98	8·64	*Iso* C_3H_7Br . .	23·88	9·06
C_3H_7Br . . .	23·56	8·74	*Iso* $C_5H_{11}Br$ . .	33·01	9·05
CH_2Br—CH_2Br.	26·83	2×8·85			

$$r_a = 8·863$$

IODINE.[2][3][4]

	$\mathfrak{M}_a.$	$r_a.$		$\mathfrak{M}_a.$	$r_a.$
CH_3I	19·25	13·58	C_4H_9I . . .	33·25	13·86
C_2H_5I . . .	24·09	13·84	*Iso* C_4H_9I . .	33·24	13·85
C_3H_7I . . .	28·73	13·91			

$$r_a = 13·808$$

SULPHUR.[5]

	$\mathfrak{M}_a.$	$r_a.$		$\mathfrak{M}_a.$	$r_a.$
SCl_2	20·55	8·51	$(C_2H_5S)_2$ . . .	36·33	8·00
S_2Cl_2	29·05	8·50	$(C_2H_5)_2S_4$ . .	53·79	8·37
C_2H_5SH . . .	19·00	7·80	C_4H_4S . . .	24·16	6·52
C_4H_9SH . . .	28·14	7·82	$(C_6H_5)_2S$ . .	58·97	9·31
$C_5H_{11}SH$ . . .	32·72	7·84	Acetal sulphide .	71·61	8·05
$(C_2H_5)_2S$ . . .	28·32	8·00	$C_6H_5N{:}CS$ . .	36·33	8·00
$(C_3H_6)_2S$ . . .	36·73	7·94	$SO(OC_2H_5)_2$ . .	31·62	5·49
$(C_7H_7)_2S$ . . .	67·42	8·04	$SO_2(OC_2H_5)_2$.	31·79	3·34

SELENIUM.[6]

	$(\mathfrak{M}_D).$	$(r_D).$		$(\mathfrak{M}_D).$	$(r_D).$
C_2H_5SeH . .	22·12	10·81	$CH_3SeC_3H_7,n.$ . .	31·46	10·81
n. C_3H_7SeH . .	26·68	10·76	$CH_3SeC_4H_9,n.$ . .	36·01	10·90
n. C_4H_9SeH . .	31·26	10·75	$C_3H_7SeC_3H_7,n.$.	40·72	11·0
$CH_3SeC_2H_5$ . .	26·76	10·85	$C_3H_7SeSeC_3H_7$.	52·38	11·33

[2] Haagen, *Pogg. Ann.*, **131**, 117 (1867); Weegman, *Zeit. Phys. Chem.*, **2**, 218, 257 (1888); Brühl, *Berichte*, **13**, 1128 (1880); *Zeit. Phys. Chem.*, **7**, 176 (1891); Conrady, *Zeit. Phys. Chem.*, **3**, 210 (1889). The examples are quoted from Brühl's later paper.

[3] Eykman, *Rec. Pays. Bas.*, **12**, 157, 268 (1893).

[4] Sullivan, *Zeit. Phys. Chem.*, **28**, 523 (1899).

[5] Wiedemann, *Wied. Ann.*, **17**, 577 (1882); Nasini, *Gazz. Chim. Ital.*, **12**, 296 (1883); Nasini and Scala, *Atti. R. Acc. dei Linc.*, 617 (1886); *Gazz.*, **20**, 367 (1890); see also Nasini in *Nuova Enciclopedia di Chimica*, I., 792 (1906); Clarke and Smiles, *Trans. Chem. Soc.*, **95**, 902 (1909).

[6] Zopellari, *Atti. R. Acc. dei Linc.*, [5] **3**, 330 (1894); especially Tschugajeff, *Ber.*, **42**, 49 (1909).

NITROGEN.[1]

Primary Aliphatic Amines.

Substance.	$\mathfrak{R}_a$.	r_a.	Substance.	$\mathfrak{R}_a$.	r_a.
Propylamine .	19·31	2·29	Isoamylamine .	28·53	2·37
Isopropylamine .	19·47	2·45	Allylamine . .	18·81	2·16
Sec. butylamine .	23·95	2·36	Ethylenediamine	18·12	2·28
Isobutylamine .	23·87	2·28	Camphylamine .	48·86	2·42

Secondary Aliphatic Amines.

Diethylamine .	24·07	2·48	α Methyl piperi-		
Dipropylamine .	33·49	2·61	dine . . .	31·16	2·63
Di-isobutylamine	42·63	2·75	β Methyl piperi-		
Di-isoamylamine	51·85	2·83	dine . . .	31·12	2·59
Piperidine . .	26·52	2·56	β Ethyl piperi-		
			dine . . .	35·50	2·40

Primary Aromatic Amines.

Aniline . . .	30·27	2·85	o Toluidine . .	34·98	2·99
m Chloro-aniline	35·32	2·99	m Toluidine . .	34·97	2·98
m Bromo-aniline	38·21	3·03	m Xyluidine .	39·68	3·12

Secondary Aromatic Amines.

Dibenzylamine .	62·92	2·25	Methyl aniline .	35·30	3·31
Tetrahydroquino-			Ethyl aniline .	40·03	3·47
line. . . .	42·37	3·44			

The few examples which are quoted in the foregoing table serve to show that the refractive equivalent of nitrogen varies according to the chemical function which this element fulfils; but in each homologous series the refractivity appears to be constant. Brühl has calculated the refractive value of nitrogen in several classes of compounds, and the more important results are shown in the annexed table.

[1] Gladstone, *Proc. Roy. Soc.*, 330 (1881); *Trans. Chem. Soc.*, **45**, 257 (1884); **59**, 298 (1891); Brühl, chiefly in *Zeit. Phys. Chem.*, **16**, 193, 226, 497, 512 (1895); **22**, 373 (1897); **25**, 576 (1898); Eykman, *Ber.*, **25**, 3069 (1892); Kannonikow, *Ber.*, **17**, *ref.* 157 (1884); Konowaloff, *Bull. Soc. Chim.*, **16**, 660 (1884); Löwenherz, *Zeit. Phys. Chem.*, **6**, 552 (1890); Perkin, *Trans. Chem. Soc.*, **55**, 750 (1889); **69**, 1152 (1896); Schmidt, *Zeit. Phys. Chem.*, **58**, 513 (1907); Trapesonzjanz, *Ber.*, **26**, 1428 (1893); Zecchini, *Atti. R. Acc. dei Lincei*, [5] **21**, 491 (1893).

TABLE XXIV.

REFRACTIVITY OF NITROGEN.

Substance.	$r_a.$	$r_D.$	Substance.	$r_a.$	$r_D.$
Ammonia	2·32	2·50	Tertiary arom. amines	4·10	4·36
Hydroxylamine . .	2·35	2·51	Aliphatic nitrile . .	3·17	3·05
Hydrazine . . .	2·32	2·47	Aromatic ,, . .	3·82	3·79
Primary aliph. amines	2·31	2·45	Sec. aliphatic amides	2·23	2·27
Secondary ,, ,,	2·60	2·65	Tert. ,, ,,	2·63	2·71
Tertiary ,, ,,	2·92	3·00	Aliphatic aldoximes} and ketoximes }	3·92	3·93
Primary arom. amines	3·01	3·21			
Secondary ,, ,,	3·40	3·59	Aliphatic nitro group	6·65	6·71[1]

The refractive powers of several other elements have been studied, but it is of little use here to reproduce them since the values obtained are not constant, and the data on which they are based are too few to permit the effect of constitution to be clearly followed. For the refractive powers of compounds of phosphorus,[2] tellurium,[3] silicon,[4] tin,[5] lead,[5] boron,[6] antimony,[7] and mercury,[7] the reader should consult the original literature.

§ 13. THE CALCULATION OF THE MOLECULAR REFRACTIVITY OF AN ORGANIC COMPOUND

According to the process suggested by Landolt, it is possible, with the aid of the refractivities of the various elements, to calculate the molecular refractive power of a compound; but in doing this it is evident that we must use the particular

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[1] These numbers refer to the whole group.

[2] Zecchini, *Zeit. Phys. Chem.*, **12**, 505 (1893) ; **16**, 242 (1895).

[3] Pellini and Menin, *Gazz. Chim. Ital.*, **30**, II., 45 (1900).

[4] Abati, *Gazz. Chim. Ital.*, **27**, II., 437 (1897) ; *Zeit. Phys. Chem.*, **25**, 253 (1898).

[5] Ghira, *Atti. R. Accad. d. Lincei*, [5] **3**, 1, 322 (1894).

[6] Ghira, *Atti. R. Accad. d. Lincei*, [5] **2**, 1, 312 (1890).

[7] Ghira, *Atti. R. Accad. d. Lincei*, [5] **3**, 1, 297 (1894).

values of the elements for the conditions under which they occur in the substance. The process is, therefore, at present limited to substances containing only carbon, hydrogen, oxygen, nitrogen, and the halogens, since the refractivity of other elements, such as phosphorus and sulphur, are very imperfectly known. Even with nitrogen, which has been so carefully studied by Brühl, the process is likely to give unsatisfactory results unless confined to the class of substance from which the atomic refractivity has been deduced. The careful work of Conrady and of Eykman has further shown that the refractive effect of carbon varies if this element is united to hydrogen and oxygen only, or to two other carbon atoms. Generally speaking, however, the method gives very good results with simple compounds containing carbon, hydrogen, and oxygen. The following table contains a selection of the data usually employed in the calculation.

TABLE XXV.

Element.	n formula.		n^2 formula.	
	$R_a.$	$R_D.$	$r_a.$	$r_D.$
Carbon singly bound occurring alone, C°	5·00	4·71	2·365	2·592
Carbon singly bound, C' . . .				2·501
Hydrogen, H	1·30	1·47	1·103	1·051
Hydroxyl oxygen, O'	2·80	2·65	1·506	1·521
Ethereal oxygen, O<			1·655	1·683
Ketonic oxygen, O″	3·40	3·33	2·328	2·287
Ethenoid linkage, I=	2·40	2·64	1·836	1·707
Acetylene linkage, I≡	—	—	2·27 or 2·48	2·10
Chlorine	9·79	10·05	6·014	5·998
Bromine	15·38	15·34	8·863	8·927
Iodine	24·87	25·01	13·808	14·12
Sulphur, S<	—	—	8·0	—

Some illustrations of the process follow.

LACTIC ACID.	CYCLOPENTANONE.

$CH_3CHOHCOOH$ or $C_3H_6O'_2O''$ $\qquad$ $(CH_2)_4CO$ or C_5H_8O''

$$R_\alpha \quad C_3 = 15 \cdot 00 \qquad\qquad r_D \quad C_5 = 12 \cdot 505$$
$$H_6 = 7 \cdot 80 \qquad\qquad\quad H_8 = 8 \cdot 408$$
$$O'_2 = 5 \cdot 60 \qquad\qquad\quad O'' = 2 \cdot 287$$
$$O'' = 3 \cdot 40$$
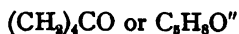
M_α (calculated) $= 31 \cdot 87$ $\qquad$ $\mathfrak{M}_D$ (calculated) $= 23 \cdot 200$

M_α (observed) $= 31 \cdot 87$ $\qquad$ $\mathfrak{M}_D$ (observed) $= 23 \cdot 197$

ETHYL MALEATE.

$H_5C_2OOCCH = CHCOOC_2H_5$ or $C_8H_{12}O'_2O''_2I^=$

$$R_\alpha \quad C_8 = 40 \cdot 00$$
$$H_{12} = 15 \cdot 60$$
$$O_2< \ = 5 \cdot 60$$
$$O''_2 = 6 \cdot 80$$
$$I^= \ = 2 \cdot 40$$

M_α (calculated) $= 70 \cdot 40$

M_α (observed) $= 70 \cdot 43$

Having found that the value of a group may slightly vary according to the structural type of the substance in which it occurs, Eykman[1] recognized that the results obtained by the method of Landolt are not very accurate. In calculating the molecular refractive power of a substance of high molecular weight, the error involved in each atomic value is multiplied many times, so that the final result may differ by as much as two units from the observed value. Moreover, it is probable that the chief inaccuracies are caused by the atoms in the characteristic groups of the substance having slightly different values in different groups. For example, it is probable that the carbonyl-oxygen of ketones has a different refractive effect from that in the carboxyl group of acids. Hydroxyl or amino hydrogen may also differ from the hydrogen of a methylene group. To avoid this source of error Eykman suggested that the refractive values of complete groups should be used

[1] *Rec. Pays. Bas.*, **12**, 160, 248 (1893); **13**, 13 (1894); **14**, 185 (1895); **13**, 52 (1896).

instead of the refractivities of the elements. The values of M_a (Gladstone-Dale) for the more frequently occurring groups are collected in the annexed table. It should be noticed that these can only be used to obtain the refractive power of substances of the type $R'(CH_2)_nR''$ where R' and R'' are two of the given groups. When R' and R'' are directly united they have abnormal values.

TABLE XXVI.

Group.	M_a.	Group.	M_a.
—CH_2—	7·754	—CO—	8·07
—CH_3	8·81	—$CONH_2$ . . .	16·06
—C_6H_5	43·62	—CH=NOH . .	17·25
—COOH	12·15	—NH_2	7·41
—$COOC_2H_5$ . . .	27·33	—OH	4·30
—$COOCH_3$	19·58	—OC_2H_5	47·19
—$COCH_3$	17·20	—CN	9·07
— Br	14·92	—I	24·56

A few examples will serve to illustrate the process and to contrast the results with those furnished by Landolt's method.

STEARIC ACID, $CH_3(CH_2)_{16}COOH$.

Eykman's Method.		Landolt's Method.
$CH_3(CH_2)_{16}COOH$	or	$C_{18}H_{36}O'O''$
$CH_3 = 8·81$		$18C = 90·00$
$16CH_2 = 124·06$		$36H = 46·8$
$COOH = 12·15$		$O' = 2·8$
		$O'' = 3·4$
$M_a = 145·02$		$M_a = 143·00$

$$M_a \text{ (observed)} = 145·00$$

| $\Delta = 0·02$ | $\Delta = 2·00$ |

LEVULINIC ACID.

$$CH_3CO(CH_2)_2COOH \quad \text{or} \quad C_5H_8O'O''_2$$

$CH_3CO = 17 \cdot 20$	$5C = 25 \cdot 0$
$2CH_2 = 15 \cdot 508$	$8_4 = 10 \cdot 4$
$COOH = 12 \cdot 15$	$O' = 2 \cdot 8$
	$2O'' = 6 \cdot 8$
$M_\alpha = 44 \cdot 86$	$M_\alpha = 45 \cdot 0$

$$M_\alpha \text{ (observed)} = 44 \cdot 86$$

$$\Delta = 0 \cdot 0 \qquad\qquad \Delta = 0 \cdot 14$$

ETHYL SEBATE.

$$(CH_2)_8(COOC_2H_5)_2 \quad \text{or} \quad C_{14}H_{26}O'_2O''_2$$

$8CH_2 = 62 \cdot 032$	$14C = 70 \cdot 00$
$2COOC_2H_5 = 54 \cdot 66$	$26H = 33 \cdot 8$
	$2O'' = 6 \cdot 8$
	$2O' = 5 \cdot 6$
$116 \cdot 69$	$116 \cdot 2$

$$M_\alpha \text{ (observed) } 116 \cdot 69$$

$$\Delta = 0 \cdot 0 \qquad\qquad \Delta = 0 \cdot 49$$

PHENYLACETIC ACID.

$$C_6H_5CH_2COOH \quad \text{or} \quad C_8H_8O''O'I''_3$$

$C_6H_5 = 43 \cdot 62$	$8C = 40 \cdot 00$
$CH_2 = 7 \cdot 75$	$8H = 10 \cdot 40$
$COOH = 12 \cdot 15$	$O'' = 3 \cdot 4$
	$O' = 2 \cdot 8$
	$3I'' = 7 \cdot 20$
$M_\alpha = 63 \cdot 52$	$M_\alpha = 63 \cdot 80$

$$M_\alpha \text{ (observed)} = 63 \cdot 41$$

$$\Delta = 0 \cdot 11 \qquad\qquad \Delta = 0 \cdot 39$$

Sometimes the theoretical value of a very complex substance is required; in such a case it is best to take the experimental value of a compound closely allied to it in structure, and then to modify this in the necessary fashion.

CHAPTER IX

REFRACTIVE POWER (*continued*)

III. REFRACTIVITY AND CHEMICAL STRUCTURE OF ORGANIC COMPOUNDS (*continued*)

§ 14. *OPTICAL ANOMALY*[1]

FROM what has been said in the foregoing chapter it is clear that the refractive power of an element varies with the degree of saturation. We have seen that it is possible with a few elements to assign a definite refractive value for certain special conditions of saturation, and in nearly every case the refractive value increases with the degree of unsaturation. Carbon united by an acetylene bond has a larger refractive effect than ethenoid carbon, and this in turn has a greater effect than singly bound carbon. Also carbonyl oxygen has a higher value than ethereal oxygen.

There is, however, abundant evidence to show that the refractive power of a compound is influenced not merely by the presence of unsaturation, but also by the relative position of the unsaturated groups in the molecule. When a molecule contains only one unsaturated group, the value of the molecular refractive power may be said to be normal; it may then be calculated with considerable accuracy from the refractivities of the elements after making due allowance for the unsaturation. If now a second unsaturated group is introduced in a position adjacent to the first, the molecular refractive power becomes abnormal. In this case the molecular refractivity considerably differs from the value calculated with allowance

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[1] Brühl, *Ber.*, **46**, 878, 1153 (1907) ; **41**, 3712 (1908).

for the two unsaturated groups. The difference between the observed and calculated values may be called the *optical anomaly*.

If, as in most cases, the value is raised by the introduction of the second unsaturated group, the substance may be said to exhibit optical *exaltation*[1]; if it is depressed below the calculated value, the phenomenon is called optical *depression*. In most cases where the two unsaturated complexes are separated by a saturated group or groups, the anomaly disappears; the unsaturated groups are then *isolated*. It is therefore evident that unsaturated complexes in this adjacent position are in a peculiar state; they are said to be "conjugated." Brühl has applied the term "conjugated" to any arrangement of unsaturated groups which exert a mutual influence.

Chemical. evidence of the abnormal state of adjacent unsaturated groups is not wanting. Thiele[2] pointed out that many substances containing two adjacent ethylene bonds behave as though the residual affinity of the unsaturated groups was attached to the extreme atoms of the system. Thus many substances containing the group

$$-CH=CH-CH=CH-$$

yield on reduction

$$-CH_2-CH=CH-CH_2-$$

and not

$$-CH_2-CH_2-CH=CH-$$
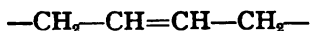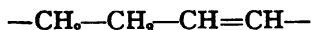
as might be expected from the saturation of one individual ethenoid linkage. In order to explain this peculiar behaviour Thiele imagined that each unsaturated carbon atom is endowed with residual affinity, and he further assumed that the residual affinities of the carbon atoms which unite the two ethenoid systems satisfy one another. To represent this condition graphically, the formula would be written as—

$$X-CH=CH-CH=CH-Y$$

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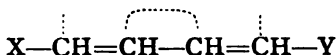
[1] Nasini, *Gazz.*, **37**, II., 55 (1907).
[2] Thiele, *Ann.*, **306**, 89 (1899); **311**, 248 (1900); **319**, 129 (1901).

where the dotted lines represent the residual affinities, or, as they were called by Thiele, the partial valencies. Thus the end carbon atoms of the group would act as the chief centres of unsaturation, and any other atoms combining with the system must unite with them.[1] When the unsaturated groups are isolated, the additive reactions of the substance are normal. Anomalous behaviour has also been observed[2] with the $\alpha-\beta$ unsaturated ketones, which contain a carbonyl group in conjugation with the ethenoid linkage, thus—

$$-CH=CH-CO-CH_2-$$

In these substances the reactivity of the ethylene linkage is abnormally increased, whilst that of the carbonyl group is lessened. Additive reagents which, in normal ketones, react with the carbonyl group, now attack the ethylene bond. For example, the reduction of benzal acetone[3] with aluminium amalgam in ethereal solution, proceeds as follows :—

$$2C_6H_5-CH=CH-CO-CH_3 \longrightarrow \begin{array}{l} C_6H_5-CH-CH_2-CO-CH_3 \\ | \\ C_6H_5-CH-CH_2-CO-CH_3 \end{array}$$
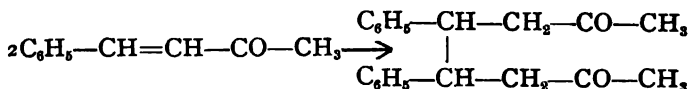
Other reagents, such as hydrocyanic acid, ammonia, hydroxylamine and mercaptan react in a similar manner. Phorone and ammonia[4] unite as follows :—

$$(CH_3)_2C=CH-CO-CH=C(CH_3)_2 + 2NH_3 = \\ \begin{array}{ccc} (CH_3)_2C-CH_2-CO-CH_2-C(CH_3)_2 \\ | & & | \\ NH_2 & & NH_2 \end{array}$$
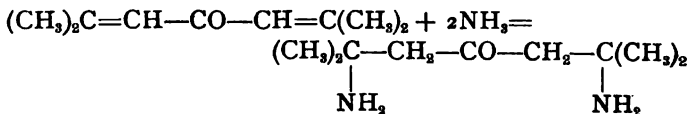
yielding triacetone diamine. Mesityloxide combines with hydrocyanic acid[5]—

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[1] It has been found that when the groups X and Y, or the two entrant atoms, are very different from one another the reaction may proceed normally.

[2] Harries, *Ann.*, **330**, 185 (1904).

[3] Harries and Eschenbach, *Ber.*, **29**, 383 (1896).

[4] Hentz, *Ann.*, **203**, 336 (1880).

[5] Lapworth, *Trans. Chem. Soc.*, **85**, 1218 (1904).

$$(CH_3)_2C=CH-COCH_3 + HCN \rightarrow$$
$$(CH_3)_2-\underset{\underset{CN}{|}}{C}-CH_2-CO-CH_3$$
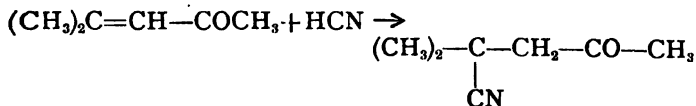
with hydroxylamine[1] under certain conditions, giving

$$(CH_3)_2\underset{\underset{NHOH}{|}}{C}-CH_2-CO-CH_3$$
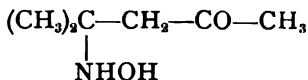
and with sodium bisulphite[2] forming the sulphonate

$$(CH_3)_2\underset{\underset{SO_3Na}{|}}{C}-CH_2-CO-CH_3$$
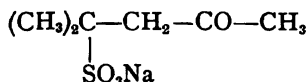
When the carbonyl and ethenoid groups are isolated as in the β–γ ketone

$$CH_2=CH-CH_2-CO-CH_3$$
Allyl methyl ketone

or the γ–δ ketone
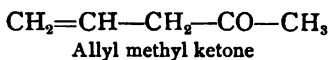
$$CH_2=CH-CH_2-CH_2-CO-CH_3$$
Allyl acetone
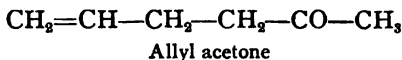
the former group resumes its normal activity. Ketones of the β–γ or γ–δ type may be reduced to the unsaturated secondary alcohols, and this reaction is unknown with the α–β derivatives. Moreover hydroxylamine reacts normally with the β–γ[4] and γ–δ[5] ketones forming oximes.

The two systems

$$-CH=CH-CH=CH-$$
and
$$-CH=CH-C=O$$
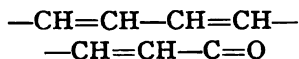
show a striking optical anomaly, so that evidence from the physical side is found to support chemical experience.

[1] Kerp and Müller, *Ann.*, **299**, 213, 217 (1898).
[2] Pinner, *Ber.*, **16**, 592 (1892).
[3] Harries, *ibid*.
[4] Blaise, *Bull. Soc. Chim.*, [3] **33**, 39–43 (1905).
[5] Harries, *Ann.*, **330**, 185–279 (1904).
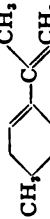
We may now examine the optical data on which the assumption of conjugation is based. Inspection of the tables on the annexed slip will show that with a substance containing two unsaturated groups adjacent to one another, the observed molecular refractive power is considerably larger than that calculated from the " normal " values of the elements ; in most cases the divergence is about one unit. It is further evident that when these groups are isolated, the observed refractivity approximates to the calculated value ; here the maximum difference is o·30 units in the limonenes and methyl heptenone. This " exalting " effect of conjugation perhaps may be better appreciated if the observed values of isomerides containing conjugated and isolated unsaturation be compared. A few comparisons are shown in Table XXVIII ; the column under Δ contains the differences between the molecular refractivities of the isomerides.
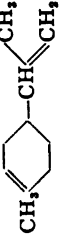
A few of the substances quoted contain unsaturated groups in what may be called multiple conjugation ; that is to say, more than two groups may be conjugated as in hexatriene $\overset{(1)}{C}H_2{=}CH{-}\overset{(3)}{C}H{=}CH{-}\overset{(5)}{C}H{=}CH_2$, where the unsaturated bonds in positions 1 and 5 are each conjugated with that in position 3. It may be noted that such compounds usually show a greater exaltation than those with simple conjugation, though the increase is by no means proportionate to the number of groups in conjunction. For example, the exaltation of mesityl oxide is o·73, whilst that of the doubly conjugated phorone is 2·66, or nearly three times as great ; and on the other hand, the exaltation of hexatriene (2·06) is only about twice that of isodiallyl (o·98). It seems premature further to discuss the effect of constitution on the magnitude of exaltation, since it is doubtful whether all the measurements quoted are sufficiently accurate. At the same time it should be observed that in a few instances the degree of exaltation and unsaturation have been found to run parallel.

In addition to these types of conjugated unsaturated groups, many others have been investigated by the optical method, but in several cases the evidence from the chemical

TABLE XXVII.

ETHENOID LINKAGES.

In Conjunction.

Substance.	M_α (obs.).	M_α (calc.).	Δ	M_r-M_α (obs.).	M_r-M_α (calc.).	Δ
Isodiallyl [1] CH₃CH:CH—CH:CH—CH:CHCH₃	29·87	28·89	+0·98	1·46	1·05	0·41
Hexatriene [4] CH₂=CH—CH=CH—CH=CH₂	30·58	28·52	+2·06	—	—	—
Tropilidene [1] CH—CH=CH⟩CH₂ ‖ CH—CH=CH	31·57	30·89	+0·68	1·62	1·25	0·37
Δ 1·5 m. Menthadiene [2] CH(CH₃)₂	(D) 45·94	45·24	+0·70	—	—	—
Δ 1·3 p. Menthadiene [2] CH(CH₃)₂	(D) 46·17	45·24	+0·93	—	—	—
Δ 3·8 (9) p. Menthadiene [2]	(D) 46·98	45·24	+1·74	—	—	—
	(α) 45·80 [3]	44·97	+0·83	—	—	—

Isolated.

Compound		A	B	C	D	E	F
Diallyl [1]	$CH_2{=}CHCH_2CH_2CH{=}CH_2$	45·11	45·09	−0·14	—	1·43	0·02
l Limonene [3]	(structure, with CH_3, $-CH\langle^{CH_3}_{CH_2}$)	45·26	44·97	+0·29	1·45	1·43	0·02
d Limonene [3]		45·26	44·97	+0·29	1·45	1·43	0·02
Dipentene [3]		45·27	44·97	+0·30	1·45	1·43	0·02
Carvestrene [2]	(structure, $CH{=}CH_2$, CH_3)	(D) 45·10	45·24	−0·14	—	—	—
Silvestrene [2]	(structure)	(D) 45·22	45·24	−0·02	—	—	—
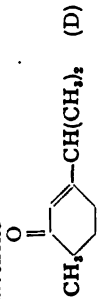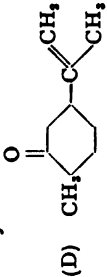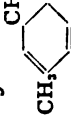
ETHENOID LINK AND CARBONYL GROUP.

In Conjunction.

Compound		A	B	C	D	E	F
Mesityl oxide [5]	$(CH_3)_2C{=}CH{-}CO(CH_3)$	30·13	29·39	+0·74	1·27	0·91	0·36
Phorone [5]	$(CH_3)_2C{=}CH{-}\underset{\parallel\ O}{C}{-}CH{=}C(CH_3)_2$	45·39	42·73	+2·66	—	—	—
Ethyl crotonate [6]	$CH_3CH{=}CH{-}CO(OC_2H_5)$	31·49	31·05	+0·44	1·11	0·93	0·18
Angelic acid [7]	$CH_3CH{=}C(CH_3)COOH$	26·95	26·32	+0·63	—	—	—
α-β Hexenic acid [7]	$\dots CH_2CH_2CH_2CH_2CH{=}CHCOOH$	31·56	30·88	+0·68	—	—	—

TABLE XXVIII.

COMPARISON OF ISOMERIDES.

Conjugated.	$\mathfrak{M}_a$ (obs.).	Δ.	$\mathfrak{M}_a$ (obs.).	Isolated.
Isodiallyl $CH_3CH=CH-CH=CHCH_3$	29·87	1·10	28·77	Diallyl $CH_2=CH-CH_2CH_2CH=CH_2$
α-β Hexenic acid $CH_3CH_2CH_2CH=CHCOOH$	31·56	0·57	30·99	β-γ Hexenic acid $CH_3CH_2CH=CHCH_2COOH$
Carvenone $CH_3\!-\!\!\bigcirc\!\!-CH(CH_3)_2$ (D)	46·92	1·08	45·84	Dihydrocarvone (D)
Angelic acid $CH_3CH=CCOOH$ / CH_3	26·95	0·77	26·18	γ-δ Pentenic acid $CH_2=CH-CH_2-CH_2COOH$
Δ 1·5 m Menthadiene $CH(CH_3)_2$ (D) CH_3	45·94	0·72	45·22	Silvestrene (D)

side is not so complete. The majority of these show exaltation similar to that already noticed with the diethenoid and ethenoid-carbonyl systems. A few further examples of aliphatic compounds showing exaltation are collected in the table below. The contrast between isolation and conjugation is shown in only one instance : the acetylene-carbonyl group

$$—C \equiv C—C = O$$

The extreme right-hand column of the table contains the dispersion anomaly.

TABLE XXIX.

Substance.	$\mathfrak{M}_\alpha$(obs.).	$\mathfrak{M}_\alpha$(calc.).	Δ	$\Delta \, \mathfrak{M}_\alpha - \mathfrak{M}_\gamma$.
Ethyl propiolate [1]				
$CH \equiv CCOOC_2H_5$	25·12	24·62	+0·50	—
Ethyl $\Delta\gamma$ butinene carboxylate [1]				
$HC \equiv C—CH_2CH_2COOC_2H_5$.	33·82	33·79	+0·03	—
Amyl propiolic acid [3]				
$CH_3(CH_2)_4C \equiv C . COOH$ . .	39·86	38·48	+1·38	—
Amyl propiolic nitrile [2]				
$CH_3(CH_2)_4C \equiv C—C \equiv N$ . .	38·40	36·71	+1·69	+0·28
Pyruvic aldoxime [2]				
$CH_3CO—CH = NOH$ . . .	21·39	20·39	+1·00	+0·54
Mesityl oxime [4]				
$(CH_3)_2C = CH—C(CH_3) = NOH$	34·49	33·59	+0·90	+0·39
Cyanogen [4]				
$N \equiv C—C \equiv N$.	12·26	11.08	+1·18	+0·08

It is especially interesting to notice that with two of these conjugated systems a connection has been found to exist between the magnitude of the exaltation and the chemical nature of the substance. Moureu[5] showed that in derivatives of acetylene the anomaly increases with the negative character

[1] Perkin, *Trans. Chem. Soc.*, **91**, 835 (1907).

[2] Moureu, *Ann. Chim. Phys.*, [8] **7**, 536 (1906). In the calculated refractivities the acetylene bond has the value obtained from caprylidene and oenanthylidene (see p. 268).

[3] Muller and Bauer, *Journ. de Chim. Phys.*, **1**, 190 (1903).

[4] Brühl, *Ber.*, **40**, 884 (1907)

[5] Moureu, *Ann. Chim. Phys.*, [8] **7**, 536 (1906).

of the substituting group. An illustration is afforded by the
following substances.

TABLE XXX.

Substance.	$\mathfrak{M}_\alpha$ (obs.)	$\mathfrak{M}_\alpha$(calc.).	Δ	$\Delta\,\mathfrak{M}_\alpha - \mathfrak{M}_\gamma$.
Amyl acetylene $CH_3(CH_2)_4C\!=\!CH$	32·29	32·28	0·01	0·017
Amyl propiolic acetal $CH_3(CH_2)_4C\equiv C-CH(OC_2H_5)_2$	58·89	58·44	0·45	0·084
Methyl amyl-propiolate $CH_3(CH_2)_4C\equiv C-COOCH_3$.	44·14	43·20	0·94	0·221
Amyl propiolic acid $CH_3(CH_2)_4C\equiv C\,.\,COOH$ . .	39·86	38·48	1·38	0·26
Amyl propiolic nitrile $CH_3(CH_2)_4C\equiv C\,.\,C\equiv N$. . .	38·40	36·71	1·69	0·282
Phenyl propiolic nitrile $C_6H_5C\equiv C\,.\,C\equiv N$	41·92	37·97	3·95	1·672

The normal value of the acetylene linkage is here taken as
2·487 ; and this, it will be remembered, was obtained as the
mean of the experimental results from amyl and hexyl acetylene.
Amyl acetylene therefore exhibits no exaltation. The acetal,
carbomethoxyl, carboxyl, and nitrile group, with which the
acetylenic hydrogen is successively replaced, may be said to
be in the order of increasing negative characters. It is clear
that the exaltation (Δ) of molecular refractivity, and the dis-
persion anomaly ($\Delta M_\alpha - M_\gamma$) increases in the same order. It
may be further observed that by replacing the amyl group of
amyl propiolic nitrile with phenyl, the anomaly is more than
doubled.

Muller and Bauer[1] have examined a series of oximino
compounds containing the weakly acidic group $>\!C\!=\!NOH$.
The results clearly demonstrate that if these derivatives are
arranged in order of increasing anomaly, they roughly fall into
the order of increasing acidity. Here again optical exaltation
and unsaturation seem to be parallel phenomena. Muller and
Bauer obtained the following optical data.

[1] *Journ. Chim. Phys.*, 1, 190 (1903).

TABLE XXXI.

Substance.	$\mathfrak{R}_\alpha$ (obs.).	$\mathfrak{R}_\alpha$ (calc.).	Δ	Δ $\mathfrak{R}_\gamma$-$\mathfrak{R}_\alpha$
CH₃—C—CH₃ NOH	20·21	20·27	−0·06	—
CH₃—C—COOC₂H₅ NOH	31·50	31·19	0·31	0·35
CH₃—C—COOH NOH	22·45	21·90	0·55	0·20
CH₃CO—CH=NOH	21·39	20·39	1·00	0·54
CH₃CO—C—CH₃ NOH	25·93	24·97	0·96	0·37
H₅C₂OOC—C—COOC₂H₅ NOH	34·09	32·97	1·12	0·20
(HOOC)₂C=NOH	25·28	23·53	1·75	0·54
CH₃CO—C—COOC₂H₅ NOH	37·37	35·88	1·48	0·39
CN—C—COOC₂H₅ NOH	32·83	31·06	1·77	1·02
CN—C—COOH NOH	23·78	21·77	2·01	—

The substances are arranged in order of increasing exaltation, and the table is divided into four groups, in each of which are placed substances of similar exaltation and acidity. The first group contains acetoxime: a neutral substance of normal refractive power. The compounds in the second group show a slight anomaly of about 0·5 unit; they are very weak acids, their sodium salts being so extensively hydrolyzed by water that the solutions readily saponify the esters of ordinary carboxylic acids. Turning to the third division, we find substances of about the same acidity as phenol, and their exaltation is greater

than in the previous class, being about 1·0 unit. The compounds in the last section are acids of moderate strength, varying from that of carbonic acid to acetic acid. Here the acidity and exaltation are the highest of the series.

Exceptional Cases.—In the foregoing paragraphs we have seen that where unsaturated groups are in adjacent positions, there is an exaltation in refractive power. Although this is found with the majority of instances, it is by no means a general rule. Brühl[1] has shown that a few compounds containing adjacent unsaturated groups exhibit optical depression, whilst others seem to be optically normal. The clearest evidence of optical depression is afforded by certain heterocyclic compounds. Thiophene, furfurane, and pyrrol may be chosen as three typical examples.

TABLE XXXII.

Substance.	$\mathfrak{M}_\alpha$ (obs.).	$\mathfrak{M}_\alpha$ (calc.).	Δ	Δ $\mathfrak{M}_{\gamma-\alpha}$
Furfurane $O\!\!\begin{array}{c} \diagup CH\!=\!CH \\ \diagdown CH\!=\!CH \end{array}$	18·42	19·21	−0·79	—
Pyrrol $NH\!\!\begin{array}{c} \diagup CH\!=\!CH \\ \diagdown CH\!=\!CH \end{array}$	20·75	21·12	−0·37	−0·04
Thiophene $S\!\!\begin{array}{c} \diagup CH\!=\!CH \\ \diagdown CH\!=\!CH \end{array}$	24·14	25·40	−1·26	−0·04

As examples of optically normal substances containing conjugated unsaturation, Brühl quotes the α diketones and benzene with some of its simpler derivatives.

Now, in the case of benzene and toluene Brühl offers an explanation of the optically neutral state. It is well known

[1] Brühl, *Ber.*, **4**, 1157 (1907).

TABLE XXXIII.

Substance.	$\mathfrak{M}_a$ (obs.).	$\mathfrak{M}_a$(calc.).	Δ	$\Delta \mathfrak{M}_{\gamma-a.}$
Diacetyl . . . . $CH_3COCOCH_3$	20·84	20·73	+0·11	+0·02
Acetyl propionyl . . . . . $CH_3COCOCH_2CH_3$	25·30	25·31	+0·01	+0·02
Dipropionyl [1] . . . . . . $CH_3CH_2COCOCH_2CH_3$	29·96	29·87	+0·09	—
Glyoxal . . . . CHOCHO	11·86	11·68	+0·18	—
Pyruvic acid . . . . . . $CH_3COCOOH$	17·86	17·67	+0·19	+0·04
Toluene . . . . $C_6H_5 . CH_3$	30·79	30·81	−0·10	−0·11
Benzene [2] . . . . C_6H_6	25·93	26·31	−0·38	—

that benzene does not behave as an ordinary unsaturated compound; it is more stable than these towards oxidising and additive reagents. In fact, benzene is not so reactive or unsaturated as the corresponding open-chain derivative hexatriene: $CH_2=CH—CH=CH—CH=CH_2$. Thiele, with the aid of his conception of partial valency, has explained this by supposing that the residual affinities of the six carbon atoms satisfy one another. This condition may be graphically represented by the formula —
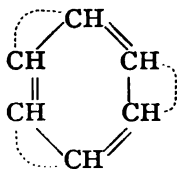
It will be noticed that since the six carbon atoms of benzene are equivalent, the partial valencies will completely compensate

[1] Anderlini, *Gazz.*, **24**, 1, 157 (1894).
[2] Brühl, *Zeit. Phys. Chem.*, 1, 349 (1887).

one another, and Brühl [1] regards this as the cause of the disappearance of the exaltation.   He styles this type of conjugation as " neutral," in distinction from the usual kind accompanying exaltation which is called " active."

It is worth noticing that the residual affinities of the above-mentioned optically depressed substances may exist in a state similar to that in benzene.   If the thiophene or pyrrol molecule be graphically represented, taking into account the partial valencies of the unsaturated atoms, we should have the following :—

$$
\begin{array}{cc}
\text{CH—CH} & \text{CH—CH} \,^{2} \\
\| \quad \| & \| \quad \| \\
\text{CH} \quad \text{CH} & \text{CH} \quad \text{CH} \\
\diagdown\diagup & \diagdown\diagup \\
\text{S} & \text{NH}
\end{array}
$$

Now, it may be observed that in accordance with these formulæ the reactivity of sulphur in thiophene, and of the imino group in pyrrol is very much less than in the corresponding open chain saturated compounds.   For example, the aliphatic sulphides readily form sulphonium iodides by addition of alkyl iodide, and with oxidizing agents they yield sulphoxides and sulphones.   Thiophene, on the other hand, does not react with alkyl iodide, and if attacked by oxidizing agents the molecule is destroyed.   Similar relations may be noted with pyrrol.[3]   It may be admitted, then, that in these substances, as in benzene, the residual affinity of the molecule forms a closed system.   Thiophene and pyrrol both are optically depressed, and turning back to benzene, it will be seen that it, also, has a slight optical depression of about 0·38 units ; and this is about the same as the depression of pyrrol which Brühl unhesitatingly places among optically depressed compounds.   The discrepancy cannot be due to experimental error, since the refractivity of benzene has been very carefully measured.   Toluene is almost normal, but here

[1] *Ber.*, **40**, 888 (1907).
[2] See Ciamician, *Ber.*, **36**, 4200 (1904).
[3] Ciamician, *ibid*.

a substituent—the CH_3 group—is introduced, and this, as we shall presently see, tends to exaltation. Also with the α diketones, which do not show the usual exaltation, there is some evidence to show that the residual affinity forms a closed system. Stewart and Baly,[1] from a spectroscopic examination of these substances, found reason for assuming that the residual affinities of the dicarbonyl system are oscillating between the two extreme phases—

$$
\begin{array}{ccc}
-C{=}C- & \rightleftarrows & -C{-}C- \\
|\ \ | & & \|\ \ \| \\
O{-}O & & O\ \ O
\end{array}
$$
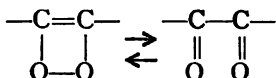
As these authors mention, it is impossible fully to represent this condition, which is essentially a dynamic one, by an ordinary chemical formula ; but it is clear from this conception of the process that in one extreme phase the residual affinities of the oxygen atoms unite to form an ordinary bond. If, then, we imagine the process to be suspended at an intermediate stage, the condition of the molecule might at that moment be represented by—

$$
\begin{array}{cc}
-C\!\!-\!\!-\!\!-C- \\
\|\ \ \ \ \| \\
O\ \ \ \ O
\end{array}
$$
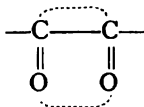
just as Thiele's formula for benzene represents the intermediate state between the extreme phases of oscillation in that substance.
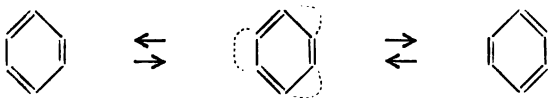
So far, then, as it is permissible to form any conclusion from these few examples, it seems that there is some connection between the presence of a closed system of residual affinity and the disappearance of the usual exaltation. But whether this be generally true or not, it is clear that the examples of optical depression which we have considered

[1] *Trans. Chem. Soc.*, **89**, 502 (1906).

afford further proof of the relations between refractive power and chemical activity.

If in these cyclic compounds the equilibrium of the neutral system of residual affinities be upset, the exaltation of ordinary conjugated unsaturation makes its appearance. This may be brought about in two chief ways; either by inserting an extra member into the ring, or by attaching an unsaturated substituent to one of the unsaturated atoms of the system. An illustration of the former process is afforded by the comparison of tropilidene with benzene. It is clear that by introducing the methylene group into the cyclic system of benzene the neutral conjugation of the latter is destroyed, and the slight depression of benzene becomes an exaltation.

$\Delta = -0.38.$
Benzene.
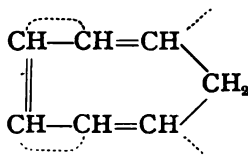
$\Delta = +0.68.$
Tropilidene.

When an unsaturated group is attached to an optically depressed molecule the balance of affinities in the cycloid system is disturbed. The substance then exhibits the usual exaltation. Taking the substitution of the vinyl group for hydrogen in benzene as an example, we may attempt to represent the change as follows :—

$\Delta = -0.38.$
Benzene.
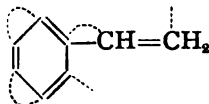
$\Delta = +0.90.$
Styrol.

It is thus evident that in styrol the vinyl group is conjugated with the aromatic nucleus.

Some further examples of the effect of substitution may be taken from heterocyclic compounds; it will be noticed that

the optical depression of the parent compound is converted by substitution into an exaltation.

Substance.	$\mathfrak{N}_a$(obs.)	$\mathfrak{N}_a$(calc.).	Δ	$\Delta\mathfrak{N}_{\gamma-a.}$
Furfurol CH—CH ‖　　‖ CH　C—CHO ＼／ O	25·12	23·89	+1·23	+0·94
aa' Dimethyl furane carboxylic ester CH—CCOOC₂H₅ ‖　　‖ CH₃CH　CCH₃ ＼／ O	44·33	43·83	+0·50	+0·31

Since the substitution products of benzene form a very large and important class of compounds, it is desirable to examine their optical behaviour in greater detail.

§ 15. *AROMATIC COMPOUNDS*

We have seen that when an unsaturated group or atom becomes attached to the benzene nucleus, the closed system of residual affinity in the latter is disturbed. From the example of styrol it is evident that the disturbance is caused by the conjugation of an unsaturated carbon atom of the benzene nucleus with the substituting group. It is, therefore, reasonable to suppose that when the residual affinity of the substituent is very weak the disturbance will only be slight, and with highly unsaturated substituents the disturbance will be greater. Optical data support this conclusion. In the appended table the substances are arranged in ascending order of exaltation, and it will be seen that the groups fall approximately into the order of saturation. At the beginning of the list we have the carbomethoxyl group (Δ = + 0·32), and at the end the acetylene group (Δ = +0·93), whilst the aldehyde

group ($\Delta = + 0\cdot66$) occupies an intermediate position. Moreover, the positions of the amino and dimethylamino groups indicate the relative strengths of their chemical activity : for conductivity measurements[1] show dimethylamine to be a stronger base than ammonia.

TABLE XXXIV.

Substance.	Formula.	$\mathfrak{M}_a$ (obs.).	$\mathfrak{M}_a$ (calc.).	Δ
Methyl benzoate[3] .	$C_6H_5COOCH_3$	37·55	37·23	+0·32
Acetophenone[5] .	$C_6H_5COCH_3$.	36·00	35·58	+0·42
Aniline[3] . . .	$C_6H_5NH_2$ . .	30·27	29·72	+0·55
Benzonitrile[3] . .	$C_6H_5C\equiv N$. .	31·32	30·75	+0·57
Nitrobenzene[3]. .	$C_6H_5NO_2$ . .	(D)32·69	(D)32·10	+0·59
Benzaldehyde[2] .	$C_6H_5CH=O$.	31·77	31·01	+0·76
Dimethylaniline[3] .	$C_6H_5N(CH_3)_2$.	40·38	39·48	+0·90
Phenyl acetylene[4].	$C_6H_5C\equiv CH$.	34·46	33·53	+0·93
Styrol[3]. . . .	$C_6H_5CH=CH_2$	35·98	35·08	+0·90

Sir W. H. Perkin[6] has performed an interesting experiment to show the effect of saturating the substituent. The value of M_a for dimethylaniline was found by experiment to be 69·86, and for hydrochloric acid 11·17. The molecular refractivity of dimethyl aniline hydrochloride calculated from the sum of these two is 81·03, but experiment gave the value 79·25. Clearly then the anomaly is reduced by saturating the dimethylamine group.

Turning to derivatives containing only saturated groups like methyl or ethyl or monovalent elements which do not readily assume a higher valency, we find that the optical condition of the benzene nucleus remains undisturbed. The following examples serve as illustration.

---

[1] See the volume in this series *Electrochemistry*, vol. i., by Dr. Lehfeldt, p. 130.

[2] Brühl, *Zeit. Phys. Chem.*, **7**, 181 (1891).

[3] Brühl, *Zeit. Phys. Chem.*, **16**, 220 (1895).

[4] Moureu, *Ann. Chim. Phys.*, [8] **7**, 536 (1906).

[5] Brühl, *Journ. Prakt. Chem.*, [2] **50**, 858 (1894).

[6] *Trans. Chem. Soc.*, **69**, 1152 (1896).

Toluene . . $\Delta = -0\cdot10$ Chlorobenzene . $\Delta = -0\cdot32$
Ethyl benzene $\Delta = -0\cdot02$ Bromobenzene . $\Delta = -0\cdot31$
Phenol . . $\Delta = -0\cdot07$ Iodobenzene . $\Delta = -0\cdot24$

Nevertheless, when these groups are accumulated in the molecule a slight tendency to exaltation is found. To illustrate this we may take the methyl group.

TABLE XXXV.

	$\mathfrak{M}_\alpha$ (obs.).	$\mathfrak{M}_\alpha$ (calc.).	Δ
Toluene [1]	30·79	30·89	−0·10
m Xylene [1]	35·73	35·45	+0·28
Mesitylene [1]	40·33	40·03	+0·28
ψ Cumene [1]	40·35	40·03	+0·30
Tetraethyl benzene [2] . .	(D) 63·92	(D) 63·26	+0·66

This behaviour indicates that even the methyl group, which is commonly assumed by chemists to be completely saturated, may, under certain conditions, possess a small amount of residual affinity. But the optical effect of this is so slight that it cannot be appreciated until multiple conjugation takes place as in mesitylene; under these conditions, as we have already seen, the optical anomaly is raised. In support of the view that the methyl group may not be completely saturated, it should be noted that Eykman [3] has recently shown that the optical value of the ethenoid linkage is slightly raised by combination with methyl or methylene. Here again, then, it seems that the increase in refractive power is due to conjugation of the methyl group with the unsaturated ethylene bond.

We may now turn to some aromatic substances in which the unsaturated substituent is not directly united to the benzene nucleus, but is attached to a saturated side chain. In such compounds the phenyl and unsaturated group are no longer directly united, and there is consequently no optical exaltation.

[1] Brühl, *Journ. Pr. Chem.*, **50**, 151 (1894).
[2] Perkin, *Trans. Chem. Soc.*, **77**, 267 (1900).
[3] *Chem. Cent.*, 1205, II., 1907.

The data collected in the following list show the effect of separating the benzene nucleus from the unsaturated substituent.

TABLE XXXVI.

Substance.	Formula.	$\mathfrak{M}_a$(obs.).	$\mathfrak{M}_a$(calc.).	Δ
Benzonitrile	$C_6H_5C\equiv N$	31·32	30·75	+0·57
Benzyl cyanide	$C_6H_5CH_2C\equiv N$	34·94	35·32	−0·38
Aniline	$C_6H_5NH_2$	30·27	29·72	+0·55
Benzylamine	$C_6H_5CH_2NH_2$	34·12	34·30	−0·18
Ethyl benzoate	$C_6H_5COOC_2H_5$	42·20	41·80	+0·40
Ethyl hydrocinnamate	$C_6H_5CH_2CH_2COOC_2H_5$	50·85	50·95	−0·10
Anethole [1]	$CH_3O \cdot C_6H_4CH=CHCH_3$	48·1	46·2	+1·9
Methyl chavicole [1]	$CH_3OC_6H_4CH_2—CH=CH_2$	46·0	46·2	−0·2
Isosafrole [1]	$CH_2O_2C_6H_3CH=CHCH_3$	47·6	45·8	+1·8
Safrole [1]	$CH_2O_2C_6H_3CH_2—CH=CH_2$	45·9	45·8	+0·1
Diphenyl [2]	$C_6H_5—C_6H_5$	51·93	50·42	+0·51
Diphenylmethane [3]	$C_6H_5CH_2C_6H_5$	55·13	55·00	+0·13
Dibenzyl [2]	$C_6H_5CH_2CH_2C_6H_5$	59·60	59·64	−0·04

On examining this list it will be observed in a few cases that optical exaltation accompanies a change in the chemical nature of the substituent. The relation is most clearly seen with the amino group. In optically normal benzylamine the amino group closely resembles that of a primary aliphatic amine ; but in aniline it assumes a different character, and the substance shows exaltation. A more interesting example is afforded by the reduction products of a and β naphthylamines. Alicyclic tetrahydro β naphthylamine (I.)

I.   II.

[1] Eykman, *Ber.*, 22, 2736 (1889) ; 23, 855 (1890).

[2] Eykman, *Rec. Pay. Bas.*, 12, 157 (1893).

[3] Perkin, *Trans. Chem. Soc.*, 69, 1152 (1895). The value 55·38 was found at 99° C, and this has been reduced by Eykman's correction for temperature.

has the molecular refractivity 45·88 [1] whilst the isomeric aromatic tetrahydro naphthylamine (II.) has $\mathfrak{M}_\alpha$ = 46·66. The calculated value for $\mathfrak{M}_\alpha$ is 45·80. In the optically anomalous "aromatic" isomeride the amino group has the abnormal character of that in aniline, whilst the normal alicyclic compound resembles benzylamine in chemical nature. It may be recalled that a similar correlation between chemical and optical properties was observed with the di-ethenoid and ethenoid-carbonyl systems. From the optical behaviour of benzyl cyanide, benzylamine and similar substances, it seems that two unsaturated groups when separated do not influence one another to any great extent. It is worth noting, however, that when three unsaturated groups are accumulated round a central saturated atom there is, in some cases, a slight exaltation, which would appear to show that conjugation may take place in spite of the intervening saturated group. This behaviour may be observed with triphenyl methane and the alkyl derivatives of cyanomalonic ester.

TABLE XXXVII.

Substance.	$\mathfrak{M}_\alpha$ (obs.).	$\mathfrak{M}_\alpha$ (calc.).	Δ
Benzene	25·93	26·31	−0·38
Toluene	30·79	30·89	−0·10
Diphenyl methane [2] . . .	55·13	55·00	+0·13
Triphenyl methane [2] . . .	79·57	79·11	+0·46
Diethyl malonate [3] . . .	62·51 (M_α)	62·41 (M_α)	+0·10
Diethyl cyano-methyl malonate [4] . . . . $CN—C(COOC_2H_5)_2$ $\quad\quad\mid$ $\quad\quad CH_2$	47·18	46·77	+0·41

[1] Brühl, *Zeit. Phys. Chem.*, **16**, 237 (1895).

[2] Calculated from the values at 99° found by Perkin, *Trans. Chem. Soc.*, **69**, 1152 (1895), with Eykman's correction for temperature; see also Smedley, *Trans. Chem. Soc.*, **93**, 376 (1908).

[3] Eykman, *Rec. Pays. Bas.*, **12**, 276 (1893). The values quoted are based on the Gladstone-Dale formula.

[4] For this and other examples see Haller, *Compt. Rend.*, **138**, 440 (1904).

TABLE XXXVIII.

Substance.	Formula.	$\mathfrak{M}_\alpha$ (obs.).	$\mathfrak{M}_\alpha$ (calc.).	Δ
Salicylic aldehyde [1]	$C_6H_4.OH.CHO$	34·03	32·52	+1·51
Benzaldehyde [1]	C_6H_5CHO	31·77	31·01	+0·76
Phenol	C_6H_5OH	27·75	27·82	−0·07
Phthalyl chloride [2]	$C_6H_4(COCl)_2$	46·81	45·53	+1·28
Benzoyl chloride [2]	C_6H_5COCl	36·79	35·92	+0·87
Ethyl phthalate [3]	$C_6H_4(COOC_2H_5)_2$	58·20	57·30	+0·90
Ethyl benzoate [1]	$C_6H_5COOC_2H_5$	42·20	41·80	+0·40
Methyl salicylic acid [1]	$C_6H_4(OCH_3)COOH$	39·80	38·74	+1·06
Anisole [9]	$C_6H_5OCH_3$	32·71	32·54	+0·17
Styrol [1]	$C_6H_5CH=CH_2$	35·98	35·08	+0·90
Phenyl butadiene [4]	$C_6H_5CH=CH—CH=CH_2$	48·00	43·86	+4·16
Stilbene [5]	$C_6H_5—CH=CHC_6H_5$	65·65	59·20	+6·45
Diphenyl butadiene [6]	$C_6H_5—CH=CH—CH=CHC_6H_5$	82·9	68·0	+14·9
Diphenyl diacetylene	$C_6H_5C{\equiv}C—C{\equiv}C·C_6H_5$	74·86	64·86	+10·0
Diphenyl hexatriene [6]	$C_6H_5CH=CH—CH=CH—CH=CHC_6H_5$	100·9	76·74	+24·16
Ethyl cinnamate [1]	$C_6H_5CH=CHCOOC_2H_5$	53·62	50·58	+3·04
Cinnamic aldehyde [1]	$C_6H_5CH=CHCH=O$	43·51	39·78	+3·73
Phenyl propiolic aldehyde [7]	$C_6H_5C{\equiv}C.CH=O$	41·50	38·22	+3·28
Cinnamylidene acetic acid [8]	$C_6H_5.CH=CH—CH=CH—COOH$	60·42	50·06	·10·36

[1] Brühl, *Zeit. Phys. Chem.*, 7, 181 (1891).
[2] Brühl, *Ann.*, 231, 1 (1886).
[3] Brühl, *Journ. Prakt. Chem.*, [2] 49, 241 (1894).
[4] Klages, *Ber.*, 40, 1768 (1907).
[5] Chilesotti, *Gazz.*, 30, 1, 149 (1900).
[6] Smedley, *Trans. Chem. Soc.*, 83, 376 (1908).
[7] Moureu, *Ann. Chim. Phys.*, [8] 7, 536 (1906).
[8] Brühl, *Zeit. Phys. Chem.*, 21, 385 (1896).
[9] Nasini and Bernheimer, *Gazz.*, 16, 84 (1886).

In concluding these few remarks on aromatic compounds it may be noted that they afford many excellent illustrations of the effect of multiple conjugation. The more important cases are col ..ted in the annexed list (p. 302). The first division contains examples of multiple substitution in the benzene ring ; and these, where possible, are compared with similar substances containing only one substituent. The compounds in the second division illustrate the effect of multiple conjugation outside the benzene nucleus.

The enormous exaltation of diphenyl hexatriene is worth special notice.

Finally, a few examples of substances containing annealed cyclic systems may be mentioned.

TABLE XXXIX.

Substance.	Temperature.	$\mathfrak{M}_\alpha$ (obs.).	$\mathfrak{M}_\alpha$ (calc.).
Naphthalene . . .	98·4°	43·93	41·65
α Naphthol	99	45·69	43·16
Bromonaphthalene . .	16·5	50·78	49·41
Anthracene	213	61·15	55·15
Phenanthrene . . .	99	61·59	56·99
Fluorene.	113	55·28	52·79
Retene	98	80·64	75·27

These compounds, without exception, show exaltation above the values calculated from the usual formulæ.

§ 16. *STEREO-ISOMERIDES*[1]

Having seen that refractive power is influenced by the relative position of unsaturation in the atomic chain of a molecule, we may now turn to stereo-isomerides and enquire

[1] Gladstone, *Ber.*, 14, 2544 (1881) ; Knops, *Ann.*, 248, 175 (1888) ; Eykman, *Rec. Pays. Bas.*, 12, 161, 268 (1893) ; Walden, *Zeit. Phys. Chem.*, 20, 377, 569 (1896) ; Brühl, *Zeit. Phys. Chem.*, 21, 385 (1896); *Ber.*, 29, 2902 (1896).

whether the actual spatial relations of the unsaturated groups have any influence on refractivity.[1]

Geometrical Isomerism.—From what has been said of optical anomaly, it may be expected that where the isomerism concerns the relative position of unsaturated groups, the two forms will have different refractive power; and, on the other hand, where all these groups are saturated, or if only one is unsaturated, the refractivity of the isomerides would be the same. This is well supported by experience. The data collected in the table refer to isomerides of the type—

$$\begin{array}{ccc} X-C-Y & \quad & X-C-Y \\ \| & \quad & \| \\ R-C-S & \quad & S-C-R \end{array}$$

The first part of the table contains three pairs of isomerides, in which only one of the groups XYRS is unsaturated; and one pair—the bromo-butylenes—is added in which all four groups are saturated. In these instances it will be seen that the refractivities of the isomeric forms lie very close to one another. With the substances of the second division at least two of the groups XYRS are unsaturated. In several instances these are carboxyl groups; in others, the phenyl or ethenoid group. Here it will be observed that the magnitude of the exaltation roughly corresponds to the difference between the isomerides. For example, the difference between ethyl maleate and fumarate is 0·67, and the exaltation of the latter is 1·2 unit; allocinnamic and cinnamic acids differ by 1·1, and the former has the exaltation of 2·7 units.

According to Brühl, it may be stated as a general rule that the more stable, higher melting and less soluble isomeride has the greater molecular refractive power. The few isomerides of the carbon-nitrogen and diazo type which have been examined also seem to obey this rule—

	$\mathfrak{M}_\alpha$		$\mathfrak{M}_\alpha$
Syn-anisaldoxime .	44·85	α Benzilmonoxime .	65·91
Anti-anisaldoxime .	45·03	β Benzilmonoxime .	66·22
Anti *m* dibromo diazobenzene cyanide .			57·17
Syn *m* dibromo diazobenzene cyanide .			55·39

TABLE XL.

Substance.	Formula.	$\mathfrak{M}_\alpha$ (obs.).	$\mathfrak{M}_\alpha$ (calc.).
Angelic acid . . . ⎫ Tiglic acid . . . ⎭	$CH_3CH{=}C(CH_3)COOH$ . . .	26·95 26·96	26·42
Oleic acid . . . ⎫ Elaidic acid . . . ⎭	$C_8H_{17}CH{=}CH(CH_2)_7COOH$ . .	86·50 86·67	—
Erucic acid . . . ⎫ Brassidic acid . . ⎭	$C_8H_{17}CH{=}CHC_{11}H_{22}COOH$ . .	105·00 105·02	—
α Bromobutylene . ⎫ β Bromobutylene . ⎭	$CH_3CH{=}CBrCH_3$	27·71 27·67	27·88
Ethyl maleate . . ⎫ Ethyl fumarate . . ⎭	$H_5C_2OOCCH{=}CHCOOC_2H_5$ . .	42·23 42·90	41·66
Ethyl citraconate ⎫ Ethyl mesaconate . ⎭	$\underset{|}{CH_3}$ $H_5C_2OOCCH{=}CHCOOC_2H_5$ . .	46·48 46·50	46·23
Cinnamic acid . ⎫ Allocinnamic acid . ⎭	$C_6H_5CH{=}CHCOOH$	44·03[1] 42·93[1]	41·29
Methyl cinnamate . ⎫ Methyl allocinnamate ⎭	$C_6H_5CH{=}CHCOOCH_3$	48·73 47·91	46·01

Cinnamylidene acetic ⎫
  acid . . . . ⎪
Allocinnamylidene ⎬
  acetic acid . . ⎭
	$C_6H_5{-}CH{=}CH{-}CH{=}CHCOOH$	58·16[1]
		
		57·25[1]
			50·06

Optical Isomerides.—The data at present available show
that optical isomerides have the same refractive power.
Measurements carried out by Walden show that the refractive
powers of amyl mesotartrate and amyl *d. l.* tartrate are
almost identical—

Amyl mesotartrate $\mathfrak{M}_\alpha = 73·54$
Amyl *dl*- tartrate $\mathfrak{M}_\alpha = 73·26$

The comparison of optical antipodes and the externally
compensated isomerides is afforded by the data on p. 306.

It may be noted that the close agreement between the
limonenes and dipentene and between silvestrene and carves-
trene does not hold between the menthadienes, which differ
by 0·49 units. Brühl[2] has stated that this exceptional
behaviour may be due to the formation of a liquid racemate.

[1] Observed in benzyl alcohol solution.
[2] *Trans. Chem. Soc.*, **91**, 115 (1907).

Substance.	$\mathfrak{M}_a$.	$\mathfrak{M}_\gamma - \mathfrak{M}_a$.
l. Limonene	45·26	1·45
d. Limonene . . .	45·26	1·45
Dipentene	45·27	1·45
d. Menthadiene . . .	45·80	—
d. *l*. Menthadiene . .	45·31	—
Silvestrene	(D) 45·22	—
Carvestrene	(D) 45·10	—

§ 17. THE APPLICATION OF THE RELATIONS TO CHEMICAL PROBLEMS

In the previous pages of this chapter we have reviewed the relations between constitution and refractive power, and we may now take a brief survey of the methods by which chemists have turned these relations to practical use.[1]

Refractive power may be said to afford definite evidence of the presence and number of ethenoid linkages in a substance. If the molecular refractivity of a carbon compound agrees with the value obtained from the sum of the atomic refractivities, it may be inferred that the substance is saturated; but if they differ by approximately 1·8 ($r_a I =$), there is one ethenoid linkage; if by 3·6, two; and so on. In simple cases like this, where chemical information is usually definite and leaves no room for doubt as to the degree of unsaturation of the substance, the method has not been extensively applied. But in compounds like the terpenes, it is often very difficult to determine by chemical means whether a substance contains an ethenoid linkage or one of the smaller saturated cyclic systems; *e.g.* whether

I.   or   II.
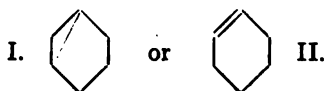
[1] See also *Die Alicyclische Verbindungen*, O. Aschan; *Die Aetherische Oele*, Semmler, vol. i. (1906).

is the correct formula for the substance. From what has been said of the effect of ring-formation, it will be remembered that a substance containing a bicyclic system (I.) may have a somewhat higher refractivity than that calculated, but the difference is never as large as the increment caused by the double bond (as in II.). It is now generally recognized that in problems of this nature a knowledge of the refractive power may prove of very great service.

Refractive power may further be utilized to ascertain the relative positions of unsaturated groups in a molecule. Chemical evidence on this question in many cases cannot be obtained. Here use may be made of the fact that adjacent unsaturated groups cause an exaltation, so that it is only necessary to compare the calculated with the observed refractivity; and if the latter be abnormally high, it may be concluded that the unsaturated groups in question are in adjacent positions.

We may now consider a few of the more important examples of the application of these principles. Kannonikow[1] measured the molecular refractivity of camphor, and found that it agrees with the value calculated for a saturated ketone, $C_{10}H_{16}O$. This confirms the formula—

$$CH_2\text{---}CH\text{---}CH_2$$
$$CH_3 . C . CH_3$$
$$CH_2\text{---}C\text{------}CO$$
$$CH_3$$
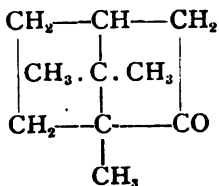
$$M_a \text{ (obs.)} = 74\cdot4$$
$$M_a \text{ for } C_{10}H_{16}O'' = 74\cdot2$$

which has since been established for that substance. Tschugaeff[2] showed that the molecular refractive power of tanacetone is 44·78 (M_a), whereas the calculated value for a saturated ketone $C_{10}H_{16}O$ is 44·11, and for the substance with one ethylene bond 45·82. Tanacetone cannot therefore be unsaturated, and since the excess of o·6 units over the saturated value is about

[1] *Journ. für Prakt. Chem.*, (II.) **32**, 504 (1885).
[2] *Ber.*, **33**, 3122 (1900).

equal to the increment for the trimethylene ring, hence the formula—

$$CH(CH_3)_2$$
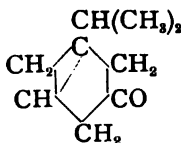
$\mathfrak{M}_{(d)}$ (obs.) $= 44\cdot78$
$\mathfrak{M}_{(d)}$ for $C_{10}H_{16}O'' = 45\cdot11$
$\mathfrak{M}_{(d)}$ for $C_{10}H_{16}O''I = 45\cdot82$

Tanacetone.

deduced from chemical evidence [1] is confirmed.   In the same manner Semmler [2] found confirmation of the structure

$$CH(CH_3)_2$$
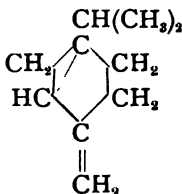
$\mathfrak{M}_{(d)}$ (obs.) $= 44\cdot8$
$\mathfrak{M}_{(d)}$ for $C_{10}H_{16} = 41\cdot8$
$\mathfrak{M}_{(d)}$ for $C_{10}H_{16}I = 43\cdot5$
$\mathfrak{M}_{(d)}$ for $C_{10}H_{16}I_2 = 45\cdot3$

Sabinene.

for sabinene. The difference between the observed refractivity and the value calculated for this formula is larger than the usual increment of the bicyclic arrangement. But here the unsaturated carbon of the ethenoid linkage is united to the trimethylene ring, and there is consequently exaltation.[3]

Further illustration of the manner in which refractivity can be applied to problems of constitution may be taken from the work of Auwers [4] on the alkylidene derivatives of dihydrobenzene. By the action of Grignard's reagent on certain derivatives of keto-dihydrobenzene (Type I.) the corresponding quinols (Type II.) may be obtained.

[1] Semmler, *Ber.*, **33**, 275 (1900) ; **36**, 4367 (1903).
[2] *Ber.*, **33**, 1464 (1900) ; **40**, 1121 (1907).
[3] See pp. 271, 272.
[4] *Ann.*, **352**, 219 (1907).

I.

CH₃ CHCl₂

O

CH₃Mg₃I
⟶

II.

CH₃ CHCl₂

OH CH₃
CH₃ CHCl₂

or

CH₃
C . Cl₂
CH₃

IIIB.

CH₃

CH₂ . CHCl₂

IV.

CH₂

IIIA.
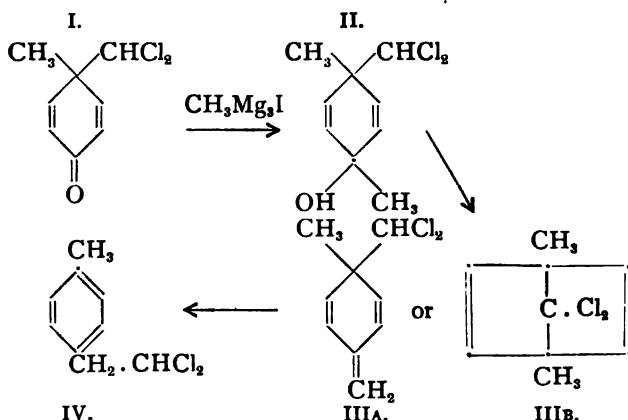
Auwers observed that these quinols easily lose water, giving unstable substances, which in turn readily undergo intramolecular change to aromatic chlorides of Type IV. That the latter are true aromatic compounds follows from their optical as well as chemical properties. Thus with the substance represented the calculated value for $\mathfrak{M}_{D}$ is 50·56, whilst experiment gave 50·14. For the unstable intermediate compound the choice lies between formulæ IIIA. and IIIB. Chemical evidence points to the former alternative, and it is upheld by the optical properties of the substance.

$$\mathfrak{M}_{D} \text{ (observed)} = 51\cdot67$$
$$\text{IIIA. } \mathfrak{M}_{D} \text{ (calculated)} = 50\cdot14$$
$$\text{IIIB. } \mathfrak{M}_{D} \text{ (calculated)} = 48\cdot43$$

The exaltation is to be expected, since in Formula IIIA. there are three ethenoid linkages in conjugation.

Allyl cyanide has been represented as

$$CH_3—CH=CH—C\equiv N \quad . \quad . \quad . \quad I.$$

where the ethenoid linkage is in the α–β position. Accordingly the substance should show exaltation, since the nitrile group and ethenoid bond are contiguous. But the calculated value for $C_4H_5I=N$ is $\mathfrak{M}_{\alpha} = 19\cdot98$, whilst experiment gives

$\mathfrak{M}_a$ = 19·75.   Hence the above formula seems incorrect, and should be replaced by

$$CH_2=CH-CH_2-C≡N. \quad . \quad . \quad . \quad . \quad II.$$

Eykman [1] has drawn the same conclusion from other data. He first showed that the effect of unsaturation varies according to the number of carbon chains attached to the ethylenic carbon atoms.   The data may here be reproduced.

Effect of unsaturation on $\mathfrak{M}_a$—

> With single substitution = −0·52
> „   double   „   = −0·37
> „   treble   „   = −0·24

The comparison—

> Propyl cyanide . . . . $\mathfrak{M}_a$ = 20·28
> Allyl cyanide . . . . $\mathfrak{M}_a$ = 19·75

shows the effect of unsaturation to be −0·53; hence the ethenoid arrangement in allyl cyanide must be as in II. ; according to the alternative formula (I.) the ethylene group has two substituents.   Similar reasoning may be used to distinguish between the two formulæ for undecylenic acid :

$$CH_2=CH(CH_2)_8COOH \qquad CH_3-CH=CH(CH_2)_7COOH$$
$$I. \qquad\qquad\qquad II.$$
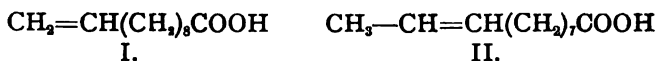
which have been respectively proposed by Kraffts [2] and by Goldsobel [3]

> Undecylic acid $C_{11}H_{22}O_2$ . . . $\mathfrak{M}_a$ = 54·48
> Undecylenic acid $C_{11}H_{20}O_2$ . . $\mathfrak{M}_a$ = 54·13

> Effect of unsaturation =   0·35

Hence the group $>C=C<$ must be doubly substituted, as in the formula of Goldsobel.

Wilsmore [4] has recently used refractive power as an aid to determine the constitution of acetyl ketene, a liquid which is

[1] *Chem. Weekblad,* **3,** 711 (1906).
[2] *Ber.,* **21,** 2730 (1883).
[3] *Ber.,* **27,** 3121 (1894).
[4] *Trans. Chem. Soc.,* **93,** 946 (1908).

obtained from ketene by polymerization. In order to decide whether the substance has the cyclic structure (I.) or the normal structure of acetyl ketene (II.)

$$
\begin{array}{l}
CO\text{—}CH_2 \\
| \qquad | \\
CH_2\text{—}CO \qquad\qquad CH_3CO\text{—}CH\text{=}CO \\
\quad\text{I.} \qquad\qquad\qquad\qquad\quad \text{II.}
\end{array}
$$
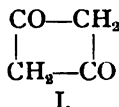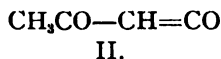
$\mathfrak{M}_D$(calc.) = 18·78. $\qquad\qquad$ $\mathfrak{M}_D$(calc.) = 20·49.

$\qquad\qquad\qquad$ $\mathfrak{M}_D$(obs.) = 20·07.

the molecular refractive power was measured. The data clearly show that the cyclic formula must be discarded in favour of the ketenic structure. It is further probable that the substance exists in the ketonic form shown above, since the value calculated for the enolic form $CH_2\text{=}C(OH)\text{—}CH\text{=}CO$, without allowance for exaltation, is 21·43.

Optical data have been brought forward in discussing the constitution of benzene. Brühl[1] showed that the refractive power of benzene and many of its simple derivatives lies very close to the values calculated from the constituent elements, with the assumption that three ethenoid linkages are present. Brühl further remarked that on changing the triple linkage of acetylene to the double one in ethylene there is a fall of 0·40 units in molecular refractive power.

Acetylene . . . . $\mathfrak{M}_D$ = 9·11
Ethylene . $\mathfrak{M}_D$ = 10·79 less (r_D2H) 2·08 = 8·71

$\qquad\qquad\qquad\qquad\qquad\qquad$ Difference = 0·40

Now, when three molecules of acetylene polymerize to one of benzene, there is a total decrease in refractive power of 1·19 units—

$$
\mathfrak{M}_D 3C_2H_2 = 3 \times 9·11 = 27·33
$$
$$
\mathfrak{M}_D C_6H_6(\text{obs.}) = 26·14
$$

$\qquad$ Difference = 1·19 = 3 × 0·40 (approx.)

and this indicates that in the process the three linkages of the

[1] *Zeit. Phys. Chem.*, **1**, 343 (1887).

acetylene molecules have been changed to three ethenoid linkages. Brühl considered that these facts definitely show that benzene has the formula proposed by Kekulé—

But from what has been discovered in recent years of the optical effect of conjugation, it seems that if the three ethenoid linkages were present as in the above formula, the refractive power of the substance should show considerable exaltation (compare hexatriene, p. 288). The fact that it does not, and instead is slightly depressed below the normal value calculated for three ethenoid linkages, shows that the unsaturated valencies of benzene are in a peculiar condition. Chilesotti[1] and Miss Smedley[2] consider that the evidence favours Armstrong's centric formula—

Benzene, however, is a substance for which the ordinary static formulæ cannot be employed satisfactorily. Collie,[3] from the general standpoint of the chemical behaviour of benzene and its derivatives, and Baly, Edwards and Stewart,[4] from spectroscopic evidence, have shown that it is probable that the carbon atoms of benzene are in continual motion, so that their unsaturated valencies do not permanently take up any definite position. The various static formulæ proposed by Kekulé, Thiele, Armstrong, and others appear to be phases in the vibration of the system.

Brühl[5] has discussed the bearing of optical data on the

[1] *Gazs.*, **30**, i. 149 (**1900**).

[2] *Trans. Chem. Soc.*, **93**, 382 (1908).

[3] *Trans. Chem. Soc.*, **71**, 1013 (1897).

[4] *Trans. Chem. Soc.*, **89**, 514 (1906) ; also Baly and Collie, *Trans. Chem. Soc.*, **87**, 1332 (1905) ; Baly and Ewbank, *ibid.*, **87**, 1347 (1905).

[5] *Zeit. Phys. Chem.*, **15**, 600 (1898).

constitution of several complex nitrogen compounds. , The most interesting case is that of nitric acid. The refractive effect of the NO_2 group in nitric acid may be obtained by subtracting from the molecular refractive power the value of hydroxyl. Thus—

$$\text{Nitric acid, } \mathfrak{M}_D(\text{obs.}) = 10\cdot00$$
$$r_D \text{ OH} = 2\cdot66$$
$$\overline{\qquad\qquad}$$
$$NO_2 = 7\cdot34$$

In the alkyl nitrates the NO_2 group has the average value $r_D = 7\cdot59$. The value of the NO_2 group in aliphatic nitro-compounds may be calculated in a similar manner, and the average is $r_D NO_2 = 6\cdot72$, which is considerably less than that obtained from nitric acid. Hence the acid cannot have the true nitro structure

$$\text{HO—N} \diagup\diagdown_O^O \quad \text{or} \quad \text{HO—N} \diagup\diagdown_O^O$$
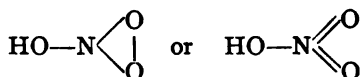
of the nitro-paraffins. Brühl further showed that in the alkyl nitrites RO—N=O, the NO_2 group has almost the same value, viz. $7\cdot44$, as in nitric acid and the alkyl nitrates; hence it was concluded that the latter must contain the —O—N=O group. They would therefore be represented by

$$\text{HO—O—N=O} \qquad\qquad \text{RO—O—N=O}$$

as derivatives of hydrogen peroxide. A remarkable confirmation of this structure has recently been obtained by Klason and Carlson,[1] who, finding that alkyl peroxide is formed as an intermediate product in the alkaline saponification of alkyl nitrates, suggest that the latter should be formulated as

$$\text{RO—O—N=O}$$
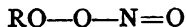
It is worth noting that Brühl does not suppose the molecule of nitric acid to be permanently fixed in this peroxidic form. From the fact that pure nitric acid is a strong electrolyte and

---

[1] *Ber.*, **39**, 2752 (1906); **40**, 4183 (1907); see also Baeyer and Villiger, *Ber.*, **34**, 755 (1901).

from its instability, he infers that there is a mobile hydrogen atom present, and that the molecule passes through several phases of which the peroxide form is only one. When the hydrogen atom is replaced by the immobile hydrocarbon radicle, as in the alkyl nitrates, it seems that the molecule definitely assumes the peroxidic state.

Tautomeric Substances.—This method of determining the constitution of a substance has been applied[1] with great success to the study of tautomeric compounds. The experiments are due chiefly to Brühl and to Perkin. By comparing the refractive power of the substance with the values calculated for the ketonic and enolic forms, it is possible to determine which of these structures the substance assumes under the conditions of experiment. The chief results are collected in the table on p. 316. The measurements were made with the pure substances at the ordinary temperature.

In the earlier experiments performed by Brühl and Perkin with substances containing two or more carbonyl groups in the β position, as in

$$-CO-CH_2-CO-CH_2-CO-$$

it was sometimes found that the refractive power is greater than that calculated for the mono-enolic form. As can be seen in the annexed table, the value occasionally falls close to that derived from the di- or tri-enolic structure, and it was then inferred that the substance exists in the multi-enolic form. This view can no longer be upheld, since it is now recognized that for an enolic structure, where the ethenoid linkage is conjugated with a carbonyl or other unsaturated group, the refractive power is " exalted." Thus with diacetyl acetone the mono-enolic form

$$CH_3CO-CH=C(OH)CH_3$$
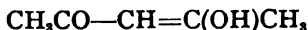
has the carbonyl group and ethenoid linkage in conjunction,

[1] Brühl, *Ber.*, **24**, 3393 (1891); **15**, 366 (1892); *Ann.*, **291**, 217 (1896); *Journ. Prakt. Chem.*, [2] **50**, 144 (1894); *Zeit. Phys. Chem.*, **30**, 1 (1899); **34**, 1 (1900); Perkin, *Trans. Chem. Soc.*, **828**, 859 (1892); Eykman, *Ber.*, **25**, 3074 (1892); Haller, *Comt. Rend.*, **138**, 440 (1904).

and hence the true refractive power of a substance of this structure would be greater than that calculated. The same may be said of the dienolic structure

$$CH_2{=}C{-}CH{=}C \cdot CH_3$$
$$\qquad \overset{\cdot}{O}H \qquad \overset{\cdot}{O}H$$
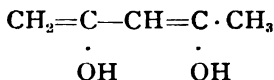
Evidently it is not correct, when the refractive power is greater than the mono-enolic value and nearly equal to that for the dienolic form, to infer that the substance has the latter structure. Moreover, it is impossible to draw any conclusion as to the relative amounts of the tautomeric forms present in a specimen under given conditions. This cannot be done until the values for exaltation in different types of conjugation have been established.

Since the refractivity method affords a means of determining which isomeric form is assumed by a substance in solution, it is possible to study the effect of various solvents on tautomeric change.[1] Wislicenus[2] has shown that the ethyl ester of formyl phenylacetic acid exists in at least two isomeric forms: the liquid isomeride

$$HOCH{=}C{-}COOC_2H_5$$
$$\qquad\quad \underset{\displaystyle C_6H_5}{|}$$
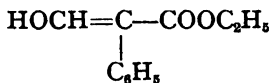
a Oxymethylene phenylacetic ester.

and the solid, which is probably the aldehyde

$$OCH{-}CH{-}COOC_2H_5$$
$$\qquad\quad \underset{\displaystyle C_6H_5}{|}$$
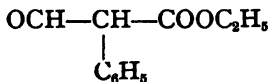
β Formyl phenylacetic ester m.p. ca 90°.

The molecular refractive power calculated for the two isomerides is—

$$\mathfrak{M}_a(\text{calc.}) = 52 \cdot 08 \text{ (enol form) or } 51 \cdot 07 \text{ (aldo form).}$$

In the pure condition the liquid ester gives $\mathfrak{M}_a = 53 \cdot 22$, thus confirming the enolic structure assigned to the substance

[1] Brühl, *Zeit. Phys. Chem.*, **30**, 1 (1899); **34**, 31 (1900).
[2] *Ber.*, **20**, 2933 (1887); **28**, 767 (1895); *Ann.*, **312**, 34 (1900).

TABLE XLI.

Substance	Formula	$\mathfrak{M}_\alpha$ (obs.)	$\mathfrak{M}_\alpha$ (calc.) for		Inferred structure.
			Ketonic.	Enolic.	
Pyruvic acid	CH₃COCOOH	17·86	17·67	18·68	ketonic
Ethyl acetoacetate . . .	CH₃COCH₂COOC₂H₅ .	31·89	31·53	32·55	ketonic
Levulinic acid	CH₃COCH₂CH₂COOH .	26·79	26·81	27·83	ketonic
Ethyl α acetyl propionate .	CH₃COCH—COOC₂H₅ .	35·55	36·10	37·12	ketonic
	└CH₃				
Methyl α acetyl isobutyrate .	CH₃CO.C—COOCH₃. / └(CH₃)₂	36·27	36·10	37·12	ketonic
Acetyl ethyl malonic ester .	CH₃COC(COOC₂H₅)₂ / └C₂H₅	56·22	56·16	57·18	ketonic
Acetyl malonic ester . .	CH₃COCH(COOC₂H₅)₂ .	48·60	47·02	48·04	enolic
Ethyl oxaloacetate . .	COOC₂H₅.COCH₂COOC₂H₅ .	43·38	42·45	43·46	enolic
Ethyl acetone dicarboxylate .	C₂H₅OOC.CH₂COCH₂COOC₂H₅	47·64	47·02	48·04	(partially enolic)
Diacetyl malonic ester .	(CH₃CO)₂C.(COOC₂H₅)₂ .	58·61	56·29	{ mono. 57·30 / dienol. 58·31 }	enolic
Acetone oxalic ester . .	CH₃COCH₂CO.COOC₂H₅ .	39·08	36·22	{ mono. 37·24 / dienol. 38·25 }	enolic
Acetyl acetone. . . .	CH₃COCH₂COCH₃ . .	27·45	25·31	{ mono. 26·32 / dienol. 27·33 }	enolic
Methyl acetyl acetone . .	CH₃COCH—COCH₃ . / └CH₃	39·75	29·88	{ mono. 30·89 / dienol. 31·90 }	enolic
Diacetyl acetone . . .	CH₃COCH₂COCH₂COCH₃ .	64·40[1]	58·2[1]	{ mono. 59·9[1] / dienol. 61·6 / trienol. 63·3 }	enolic
β Amino crotonic ester . .	CH₃C=CHCOOC₂H₅ / NH₂	36·81	{ amino form . . 34·48 / imino form less than this	}	amino

Substance		$\mathfrak{M}_\alpha$ (obs.).	$\mathfrak{M}_\alpha$ (calc.) ketonic.	$\mathfrak{M}_\alpha$ (calc.) enolic.	Structure.
α Oxymethylene phenylacetic ester	$\mathrm{CHOH{=}C{-}COOC_2H_5}$ / $\mathrm{C_6H_5}$	53·06	51·07	52·08	enolic
Acetate of α oxymethylene phenylacetic ester	$\mathrm{CH_3COOCH{=}C{-}COOC_2H_5}$ / $\mathrm{C_6H_5}$	63·19	—	61·50	—
Methyl cyano-acetoacetate	$\mathrm{CH_3CO{-}CHCOOCH_3}$ / CN	33·80	31·40	32·41	enolic
Methyl cyano-propionylacetate	$\mathrm{C_2H_5COCHCOOCH_3}$ / CN	38·32	35·97	36·98	enolic
Propyl cyano-acetoacetate	$\mathrm{CH_3COCHCOOC_3H_7}$ / CN	43·25	40·54	41·55	enolic

[1] The values refer to M_α at 60° C.

THE FOLLOWING WERE EXAMINED IN SOLUTION.

Substance.	Solvent.	$\mathfrak{M}_\alpha$ (obs.).	$\mathfrak{M}_\alpha$ (calc.) ketonic.	$\mathfrak{M}_\alpha$ (calc.) enolic.	Structure.
Oxymethylene camphor . $\mathrm{C_8H_{14}}{<}\genfrac{}{}{0pt}{}{C{=}CHOH}{CO}$	Chloroform, 10 per cent.	50·89	45·32	46·33 ⎫	enolic
	Methyl alcohol	50·92	45·32	46·33 ⎬	
Formyl bromocamphor . $\mathrm{C_8H_{14}}{<}\genfrac{}{}{0pt}{}{CBr.CHO}{CO}$	Chloroform, 5 per cent.	56·72	56·08	— ⎫	ketonic
	Methyl alcohol	56·32	56·08	— ⎬	

on chemical grounds. But when dissolved in ethyl alcohol the a ester gives $\mathfrak{M}_a = 51\cdot77$, a value which approximates to that calculated for the aldo form ; it is therefore probable that in this solvent at least partial transformation to the aldo-form takes place. Chloroform does not have this effect, since $\mathfrak{M}_a$ is here found to be $53\cdot42$. Since the β isomeride is solid, and is transformed by fusion to the a derivative, it is impossible from refractivity data to form any conclusion as to the nature of the pure substance ; but in alcoholic solution the refractivity is the same ($51\cdot77$) as that of the a isomeride in the same solvent. The isomeric forms of the ethyl esters of mesityl-oxide oxalic acid[1] are not so readily interchangeable as those of formyl phenyl acetic acid. The enolic a isomeride

$$(CH_3)_2C{=}CH{-}C{=}CH{-}CO{-}COOC_2\overset{\centerdot}{H}_5$$
$$\qquad\qquad\quad\ \ |$$
$$\qquad\qquad\quad OH$$
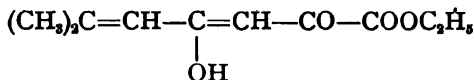
requires prolonged heating at 100° before it is completely converted to the ketonic β form—

$$(CH_3)_2C{=}CH{-}CO{-}CH_2{-}CO{-}COOC_3H_5$$
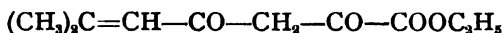
The tautomerizing action of solvents can therefore be followed by examining solutions of this substance at intervals after pre-paration. Some of the data obtained by Brühl may be quoted. It is evident that methyl alcohol ketonizes the enolic form, but

TABLE XLII.

Substance.	Condition or solvent.	$\mathfrak{M}_a$	Remarks.
a Ethyl ester—			
M.P. 21-22° . .	homogeneous	56·22	—
,,	in CHCl₃ 10%	57·74	4 days old
,,	same solution	57·91	16 days old
,,	same solution	57·74	75 days old
,,	in CH₃OH 10%	55·89	fresh
,,	same solution	55·11	7 days old
,,	same solution	51·94	61 days old
β Ethyl ester—			
M.P. 60° . . .	homogeneous	50·09	—

[1] Claisen, *Ann.*, **291**, 25 (1896).

the process is slow, the conversion not being complete in two months. Chloroform has no ketonizing action, since after seventy-five days the solution has the same value as when fresh, the refractive power being close to that of the pure enolic isomeride.

By comparing the rates of conversion of the enolic to the ketonic forms Brühl was able to obtain a comparative measure of the tautomerizing strength of various solvents. He claimed as a general rule that media with a high dielectric constant or ionizing power have a greater tautomerizing strength than those of low dielectric constant; but the recent work of Dimroth[1] and of Michael and Hibbert[2] show that this view can no longer be upheld.

In concluding this short account of the services rendered by this physical property to chemistry, notice may be taken of the method devised by Muller and Bauer[3] for the diagnosis of pseudo-acids or acids which on forming salts undergo a change in structure. Le Blanc and Rohland[4] have shown that with ordinary acids the replacement of the hydrogen ion by sodium causes a rise in molecular refractive power of about 1·64 units (N^2 formula for D line). It is clear that with pseudo-acids the value of this replacement cannot be the same, for besides the effect of salt formation there will be a further change in refractivity owing to change in structure.[5] Muller and Bauer investigated a series of oximino compounds. Some of the results are quoted below. Under Δ is shown the effect of forming the salt in the right-hand column from the corresponding acid on the left-hand side of the list. Since a few of the substances behave as dibasic acids, the salts of succinic acid are added in order to show that in normal acids the effect of forming the neutral from the acid salt is the same as when the acid is converted to the acid salt.

[1] *Ann.*, **335**, 1 (1904) ; **338**, 143 (1904).

[2] *Ber.*, **41**, 1080 (1908).

[3] *Journ. de Chim. Phys.*, **1**, 203 (1903).

[4] *Zeit. Phys. Chem.*, **19**, 261 (1896).

[5] Hantzsch has recently adopted this method in dealing with the constitution of the nitro-phenols and their salts.—*Ber.*, **43**, 95 (1910).

TABLE XLIII.

Substance.	Acid.		Δ	Salt.	
	Substance.	μ_D.		μ_D.	Substance.
Succinic acid	CH₂—COOH | CH₂—COOH	23·97	1·54	25·51	CH₂COOH | CH₂COONa
Acid. sod. succinate . . .	CH₂—COONa | CH₂—COOH	25·51	1·57	27·08	CH₂COONa | CH₂COONa
Acetoxime	(CH₃)₂C=NOH	20·21	1·47	21·68	(CH₃)₂C=NONa
Pyruvic oxime	CH₃C—COOH ‖ NOH	22·45	1·20	23·65	CH₃C—COONa ‖ NOH
Isonitroso malonic acid .	(HOOC)₂C=N.OH	25·28	2×1·27	27·81	(NaOOC)₂C=NOH
Isonitroso acetone . . .	CH₃COCH=NOH	21·39	3·74	25·13	CH₃COCH=N.ONa
Isonitroso malonic ester .	(C₂H₅OOC)₂C=N.OH	34·09	3·10	37·19	(C₂H₅OOC)₂C=N.ONa
Isonitroso camphor . .	C₈H₁₄⟨C=N.OH / CO⟩	49·14	4·01	53·15	C₈H₁₄⟨C=N.ONa / CO⟩
Isonitroso cyanacetic ester .	CN—C.COOC₂H₅ ‖ N.OH	32·83	3·29	36·12	NC—C—COOC₂H₅ ‖ N.ONa

The results show that the optical effect of salt-formation with acetoxime, pyruvic oxime and isonitrozo-malonic acid is approximately normal; hence it may be concluded that these acids have the same structure as .their sodium salts. With the remaining compounds the value of salt-formation is more than double that found with succinic acid, and it follows that the sodium salts have a different structure from that of the free acids. It may be noted that all the normal oximino compounds give colourless sodium salts, whilst the salts of the pseudo-acids are yellow.

§ 18. *DISPERSIVE POWER AND CONSTITUTION*

The idea that some relation exists between dispersive power and constitution was first entertained by Schrauf,[1] but his efforts to prove the connection were not convincing. Many years later Gladstone[2] successfully attacked the problem. Representing the specific dispersive power of a substance by

$$\frac{n_H - n_A}{d}$$

and the molecular dispersion by

$$\frac{(n_H - n_A)M}{d} \qquad \begin{array}{l} M = \text{molecular weight} \\ d = \text{density} \end{array}$$

he was able to demonstrate the additive features of the property. By comparing the molecular dispersive power of organic substances, Gladstone found that approximately constant values may be assigned to the dispersive effects of hydrogen, carbon, oxygen, and the halogens, and the sum of the dispersive effects of the atoms in a compound is approximately equal to the molecular dispersion. With the aid of his accumulated data, Brühl[3] was able more exactly to define these relations, and to elucidate the constitutive nature of the property. In all his

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[1] *Pogg. Ann.*, **116**, 193 (1862) ; **119**, 461 (1863).

[2] *Proc. Roy. Soc.*, **42**, 401 (1887); *Trans. Chem. Soc.*, **50**, 609 (1886).

[3] *Zeit. Phys. Chem.*, **7**, 140 (1891).

researches Brühl adheres to the Lorentz-Lorenz expression for refractive power, and he therefore represents the specific dispersion by

$$\frac{n_x^2 - 1}{(n_x^2 + 2)d} - \frac{n_y^2 - 1}{(n_y^2 + 2)d}$$

and the molecular dispersive power as

$$\left(\frac{n_x^2 - 1}{n_x^2 + 2} - \frac{n_y^2 - 1}{n_y^2 + 2}\right)\frac{M}{d} = \mathfrak{M}_x - \mathfrak{M}_y,$$

Brühl has calculated the dispersive effects of various atoms and modes of linkage by the process which he used for obtaining the atomic refractivities.[1] The resulting values are shown in the annexed table.

TABLE XLIV.

ATOMIC DISPERSIONS FOR THE α AND γ HYDROGEN LINES.

	$r_\gamma - r_\alpha$.	Symbol.		$r_\gamma - r_\alpha$.	Symbol.
Carbon	0·039	C	Chlorine	0·176	Cl
Hydrogen	0·036	H	Bromine	0·348	Br
Hydroxylic oxygen .	0·019	O′	Iodine	0·774	I
Ethereal oxygen . .	0·012	O<	Ethylenic bond . .	0·23	I=
Carbonyl oxygen .	0·086	O″	Acetylenic bond .	0·19	I≡

It is further claimed that the molecular dispersive power of a compound may be approximately estimated by adding together the dispersive effects of the component atoms, due allowance being made for the modes of linkage as shown in the foregoing table.   The following examples are given in order to show the degree of accuracy which is obtainable.

Ethyl Propionate.

$C_5H_{10}O''O<$
5C =	0·195
10H =	0·360
O″ =	0·086
O< =	0·012

$\mathfrak{M}_\gamma - \mathfrak{M}_\alpha$ (calc.) =   0·653
$\mathfrak{M}_\gamma - \mathfrak{M}_\alpha$ (obs.) =   0·64

Δ = +0·01

Ethyl Buyratte.

$C_6H_{12}O''O<$
6C =	0·234
12H =	0·432
O< =	0·012
O″ =	0·086

$\mathfrak{M}_\gamma - \mathfrak{M}_\alpha$ (calc.) =   0·764
$\mathfrak{M}_\gamma - \mathfrak{M}_\alpha$ (obs.) =   0·75

Δ = +0·01

[1] See pp. 258 to 268.

<table>
<tr><td>Ethyl Ether.</td><td>Isoamyl Alcohol.</td></tr>
</table>

$C_4H_{10}O <$		$C_5H_{12}O'$	
$\mathfrak{M}_\gamma - \mathfrak{M}_\alpha$ (calc.) =	0·528	$\mathfrak{M}_\gamma - \mathfrak{M}_\alpha$ (calc.) =	0·646
$\mathfrak{M}_\gamma - \mathfrak{M}_\alpha$ (obs.) =	0·55	$\mathfrak{M}_\gamma - \mathfrak{M}_\alpha$ (obs.) =	0·64
$\Delta = -0·02$		$\Delta = \pm 0·00$	

Oenanthylic Açid.		Acetyl Chloride.	
$C_7H_{14}O''O'$		$C_2H_3O''Cl$	
$\mathfrak{M}_\gamma - \mathfrak{M}_\alpha$ (calc.) =	0·875	$\mathfrak{M}_\gamma - \mathfrak{M}_\alpha$ (calc.) =	0·448
$\mathfrak{M}_\gamma - \mathfrak{M}_\alpha$ (obs.) =	0·89	$\mathfrak{M}_\gamma - \mathfrak{M}_\alpha$ (obs.) =	0·48
$\Delta = -0·02$		$\Delta = -0·03$	

These few illustrations have been chosen at random from the numerous data collected by Brühl, and it will be seen that, although the substances are of fairly low molecular weight, the agreement between calculation and experiment is not so close as with refractive power. In fact, dispersive power is more readily influenced by constitution than refractivity, and the atomic values quoted in the foregoing tables can only be regarded as rough approximations. Apart from the more constitutive nature of dispersive power, the relations shown by the property are similar to those already described with refractivity. The abnormal effect produced by adjacent unsaturated groups has been traced in the molecular dispersion of organic compounds, and many examples of the anomaly are shown in previous tables illustrating the refractive anomaly.[1] Brühl has observed that the dispersive anomaly of these substances is relatively much larger than that shown by their refractive power.

[1] Pp. 284 to 303.

CHAPTER X

THE ABSORPTION OF LIGHT

I. Introduction

§ I. *THE NATURE AND CAUSE OF ABSORPTION*

MATTER when placed in the path of a ray of solar light absorbs the energy of some of the vibrations and allows the remainder to pass on. The emergent ray, being poorer by the vibrations which have been taken up by the substance, gives a spectrum showing gaps or dark bands which indicate the wave length of the light which has disappeared. This spectrum is called the absorption spectrum, and it is characteristic for each substance under given conditions. The phenomena of absorption are exhibited both by liquids and by solids. The latter are frequently opaque, and do not allow the incident light to pass through them, but reflect the greater part at a short distance below the surface; nevertheless the thin layer of substance traversed is nearly always sufficient to develop absorption. With liquids, however, the greater portion of the light passes through the medium, and in such cases absorption is best detected in the transmitted light.

There are two distinct kinds of absorption: continuous and selective. The former is seen as a weakening effect occurring throughout whole regions in the spectrum of the transmitted light, and it is thus readily distinguished from selective absorption which takes the form of independent bands of varying width in different parts of the spectrum. It frequently happens that both kinds of absorption occur together in the same portion of the spectrum, and in this case the continuous is apt

to hide the selective absorption. The continuous absorption, however, may be weakened by lessening the number of molecules in the path of the ray of light, either by dilution with an inactive solvent, or by decreasing the thickness of layer traversed ; the selective absorption being more persistent can then be detected.

The dynamic nature' of this property was first clearly recognized by Hartley, who pointed out that absorption is caused by the movements of particles within the medium. From evidence obtained by the study of the effect of temperature and pressure on the absorption spectra of vapours, and from the fact that the intensity of continuous absorption seems to depend on the thickness of the layer traversed, Hartley considers[1] that this kind of absorption is due to a damping effect exerted on the light waves by the translatory movement of the molecules. We thus see that the relations between continuous absorption and chemical constitution are likely to be very indefinite ; and as yet very little attention has been given to the study of them. In the following pages we shall be concerned chiefly with selective absorption. From its general character Hartley inferred that this kind of absorption is caused by sub-molecular particles vibrating synchronously with the incident light waves. It is clear that if we allow a composite beam of light—such as sunlight, or that emitted by the iron arc—to traverse a medium, we can, by measuring the length of the absorbed waves, form an estimate of the vibration periods of the sub-molecular particles in this medium. The view that selective absorption is due to intra-molecular vibrations finds strong support in the work of Julius,[1] who showed that the absorption and emission spectra of simple substances are identical. The spectrum emitted by the flame of hydrogen burning in oxygen corresponds exactly to the absorption spectrum of water, and the absorption spectrum of carbon dioxide is found in the light emitted when any carbon compound is burnt in excess of oxygen.

The nature of the particles which cause selective absorption

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[1] *Trans. Chem. Soc.*, **39**, 153 (1881) ; **95**, 52 (1909) ; also *Phil. Trans.*, **208**A, 475 (1908).

also was discussed by Hartley, who at an early stage of his investigation framed the idea that the active particles are atoms or atomic complexes. . Recently, however, this view has been giving way to another which has resulted from the work of Drude[1] on the electronic theory of dispersion and absorption. According to Drude's mathematical treatment of the subject, it may be shown that vibrations corresponding to the ultra-violet and visible spectrum are due to the negatively charged electrons whose mass bears the constant ratio to the charge—

$$1\cdot5 \times 10^7 = \frac{e}{m}$$

Drude was further able to calculate the number of these electrons, and it was found that in saturated compounds this roughly corresponds to the total number of valencies of the elements present.   Hence the conclusion follows that the mobile particles which cause absorption in the visible and ultra-violet regions are valency electrons.   Baly and his colleagues have been the first to apply this notion to the study of absorption spectra from the chemical standpoint, and, as might be expected, the results are of quite a novel character. At the same time it may be observed that Hartley[2] seems still to adhere to his earlier conclusions that selective absorption in the violet region is caused by atoms or even groups.   As bearing on this question it may be mentioned that Drude has been able to show that selective absorption in the infra-red must be caused by particles whose electric charge is of opposite character to that borne by the valency electrons.   Moreover the ratio $\frac{e}{m}$ of these infra-red particles is very much smaller than $1\cdot5 \times 10^7$, indicating that their mass is immensely greater than that of the electrons.   From these considerations it follows that selective absorption in the infra-red is caused by the atoms.   In a later portion of this chapter we shall find that the conclusions formed by Drude are further confirmed by the general character of absorption in these regions.   In

[1] *Drud. Ann.*, **14**, 677, 936 (1904).
[2] *Trans. Chem. Soc.*, **95**, 53, 57 (1909).

the ultra-violet and visible portions of the spectrum the absorption is highly constitutive, in fact, the only additive relation which can be discovered is the effect caused by weighting the molecule, as in ascending homologous series, when the absorption bands are pushed towards the red. On the other hand, the infra-red absorption exhibits distinct additive features; for example, Abney was able to detect constant absorption bands due to carbon, hydrogen, and hydroxylic oxygen. This must be expected if absorption in this region is due to vibrations of atoms.

It is of some interest to inquire into the manner in which the energy of the light is distributed after it has been absorbed. We have seen that the essential condition for selective absorption is that the intra-molecular particles should be capable of synchronously vibrating with the light impulses; and it is thus a question of deciding the fate of the translatory energy conferred on these particles. Broadly speaking, it may be said that the energy may be expended in either of three ways—

1. In causing a general rise in temperature of the medium.
2. In producing fluorescent light.
3. In performing chemical changes in the medium.

From the chemist's standpoint the last-named process is very important, since it is the mainspring of the chlorophyll mechanism of plants, and is thus partly responsible for the occurrence in nature of the alkaloids, ethereal oils and other compounds upon which so much chemical research has been rightly directed. Nevertheless, organic chemists until a few years ago had neglected the study of the chemical action of light; but this line of research has been recently taken up by Ciamician, who has already obtained most interesting results. The subject will not be further developed here, since it will be fully dealt with in another volume [1] of this series.

§ 2. *MEASUREMENT OF ABSORPTION*

Many different methods have been employed for the measurement of absorption spectra, but since a full account of the apparatus and procedure adopted has been given in the

[1] *Photo-Chemistry*, by Dr. Sheppard.

volume of this series dealing with spectroscopy,[1] it is now
unnecessary to pursue the question in detail. Nearly all these
methods are based upon the same principles and differ from
one another only in the manner in which the absorption
is detected. The photographic method has given the most
accurate results, and is capable of the widest application; for
it can be used in any region of the spectrum except in the
remote infra-red. In fact, the limited use of this method in
the red region is due to the want of a photographic plate
sufficiently sensitive to rays of such great length. Abney,
however, was able to obtain a film sensitive to waves of 12,000
units length, but beyond this it seems necessary to employ the
bolometer. In dealing with absorption in the visible portion
of the spectrum several other methods are met with. Many
investigators have recorded the position of the absorption as
read on a goniometer spectroscope, some have even been
content to state the results in terms of the arbitrary scale of
the instrument, whilst yet others have confined their observa-
tions to the physiological effect of absorption, *i.e.* colour.
Then, again, some observers have measured merely the
intensity of absorption for a ray of given wave length. Photo-
graphy may now be employed with advantage in either the
ultra-violet or visible regions of the spectrum, and the develop-
ment of the method is due to Hartley.[2]

The results which are described later will be more readily
understood if an outline of the process be now given.

Substances which show a strong absorption should be
examined in solution, and the medium chosen should not exert
absorption in the region to be studied. Ethyl alcohol is the
best solvent for general purposes.

It is important to notice that although a solvent may not
exert absorption in the region of the spectrum in question, it
frequently has a physical influence on the absorption spectrum
of the solute. According to Kundt,[3] the absorption bands of

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[1] *Spectroscopy*, this series, E. C. C. Baly, p. 190.

[2] *Proc. Roy. Soc.*, **33**, 1 (1882) ; *Phil. Trans.* (1879) ; *Trans. Chem.*,
39, 153 (1881) ; **47**, 685 (1885) ; **75** (1899).

[3] *Wied. Ann.*, **4**, 34 (1878) ; for a theoretical explanation see Knob-
lauch, *Wied. Ann.*, **54**, 193 (1895).

the dissolved substance are pushed towards the red region of the spectrum by increasing the refractive index of the medium. Also chemical action between the solvent and solute may sometimes occur. For these reasons, when a comparison is being made between a series of substances, the same solvent should be employed throughout the experiments.

In order to obtain comparative results with different substances it is necessary to examine solutions of the compound of definite molecular strength. Hartley advises that the molecular weight of the substance in milligrams should be dissolved in a known volume of solvent and the solution then examined in layers of decreasing thickness, the spectrum being photographed at definite intervals of, say, one millimetre. When a thickness of one millimetre is reached the solution is diluted to a definite strength and a new series of spectra recorded in the same manner. The experiments are ceased when a nonabsorbent solution is obtained. In this way it is possible to obtain a series of spectra showing the absorption exerted by successively decreasing numbers of molecules. Hartley showed that the results are most conveniently set forth by plotting the oscillation frequencies of the limits of the absorption bands against the proportional thickness of the solution. It may be observed that the latter values are obtained by expressing each solution in terms of the thinnest layer of the most dilute mixture examined. When the points obtained by this process are joined, the absorption curve, or " curve of molecular vibrations," for the substance is formed. If fully drawn these curves may reach a length of several feet, and for this and other reasons Baly and Desch[1] recommended that the logarithms of the relative thicknesses should be used instead of the values themselves. This plan is now universally adopted.

The following illustration shows the appearance of a curve when drawn in this manner. The space above the curve shows the wave lengths of the light absorbed at various

[1] Baly and Desch, *Trans. Chem. Soc.*, **85**, 1039 (1904). See also *Spectroscopy*, this series, 414 (1905).

dilutions, and the curve itself represents the limits of the absorption. The diagram, which was obtained from photographs of camphór in alcohol, shows the presence of one band. In order to distinguish between the absorption bands of different substances it is necessary to measure their dimensions. This may be done on an ordinary spectrum photograph simply

Oscillation frequencies.

Camphor
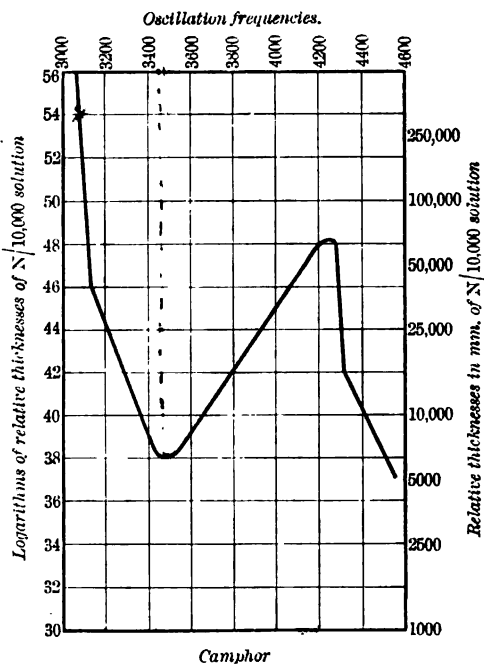
FIG. 11.

by measuring the limits of the absorbed light; but the advantage of the full absorption curve is at once apparent, for it not only shows the limits of absorption at various dilutions, but also the strength of absorption at different points within the band. In the case of camphor the strongest absorption occurs at about 3500 units of oscillation frequency. This region of the curve, which represents the portion of the band most

resistant to dilution, is usually referred to as the " *head*" of the band.   The "*persistence*" of the band represents its power of resisting dilution, and it is measured by the depths of the band, which in the case of camphor extends over ten units—from 38 to 48—on the logarithmic scale of relative thicknesses of solution.

II. Absorption Spectra and the Chemical Constitution of Organic Compounds

§ 3. *HISTORICAL*

The study of the relations between absorption and constitution may be said to date from 1879, when Hartley [1] published his first paper dealing with this subject.   Before this date the only mention of the question seems to have been that made by Miller,[2] who stated that he could find no reason to suspect any connection between the " diactinic power" of matter and its chemical nature.   In 1879, Soret and Rilliet [3] published their investigation of the alkyl nitrates ; but the authors confined their attention to these substances, and were content to record the fact that the ultra-violet absorption shifts towards the visible portion of the spectrum as the homologous series is ascended.   Since that date numerous chemists have entered this field of research, but Hartley, whose investigations have continued for thirty years, must be regarded as the founder of this important subject.

Hartley, although fully aware of the dynamic nature of this property, dealt mainly with the structure of the chemical molecule as represented by the usual static formula.   But in recent years, since the advent of the electronic theory, Baly, Desch, and Stewart have begun the study of the relations between intra-molecular dynamics and absorption.

[1] *Proc. Roy. Soc.*, **28**, 223 (1879).

[2] *Phil. Trans.*, **152**, 861 (1862).

[3] *Compt. Rend.*, **89**, 747 (1879).

§ 4. *GENERAL CHARACTER OF THE RELATIONS*

Before examining the numerous relations which have been observed between chemical constitution and absorption, we may take a brief survey of the general character of the property. The constitutive nature of absorption is to be anticipated from what has been previously said of the cause of the selective absorption of light in the visible and ultra-violet regions. With regard to the additive side of the property, it cannot be said that much is known, but it seems almost certain that the study of replacements and types of isomerism would be of little value. Hartley[1] examined the influence of position isomerism in the benzene nucleus, but he could find no general rule connecting this with absorption. The only additive feature which has been clearly recognized is the effect of homology. It has been found that in simple substances like the alkyl nitrates,[2] alcohols,[3] and amines,[4] the addition of methylene causes the absorption bands to shift towards the red portion of the spectrum, but no quantitative relation can be stated.

From the general results of work on this question it is clear that the effect of rising homology is similar to that found with other constitutive physical properties, such as melting-point, in which the effect decreases on ascending the series until it may finally vanish. With simple compounds such as those mentioned, the effect on absorption can be readily observed; but with compounds of high molecular weight it cannot be detected; in fact, Dobbie and Lauder[5] have shown that homologous alkaloids, such as codeine and morphine, quinine and cupreine, have identical absorption curves.

According to the experiments of Dobbie and Lauder[6] it may be stated as a general rule that a given substitution has a

[1] *Trans. Chem. Soc.*, **53**, 641 (1888).

[2] Soret and Rilliet, *Compt. Rend.*, **89**, 747 (1879).

[3] Hartley and Huntington, *Proc. Roy. Soc.*, **223** (1879).

[4] Russell and Lapraik, *Trans. Chem. Soc.*, **39**, 168 (1881).

[5] *Trans. Chem. Soc.*, **83**, 610 (1903).

[6] *Loc. cit.*, 612.

less effect on the absorption curves of complex bodies than on those of simpler compounds. For example, the simple benzene derivatives, piperonylic and veratric acids

Piperonylic acid.   Veratric acid.
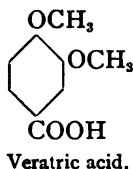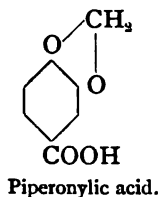
have somewhat different absorption curves, whilst the complex alkaloids

Tetrahydroberberine.   Corydaline.
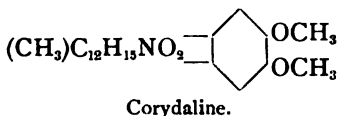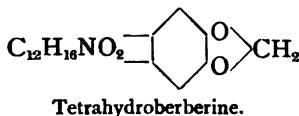
tetrahydroberberine and corydaline, which bear almost the same relations to one another, have very nearly the same absorption curve. Moreover, styrol and benzoic acid exhibit very different spectra, although the absorption curves of cinchonine and cinchotenine

$C_6H_5CH{=}CH_2$ C_6H_5COOH
Styrol.   Benzoic acid.

$C_{17}H_{19}N_2O \cdot CH{=}CH_2$ $C_{17}H_{19}N_2O \cdot COOH$
Cinchonine.   Cinchotenine.
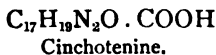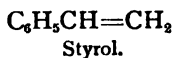
are practically identical.

The question whether it is ever possible to pick out the absorptive effect of individual groups is very difficult to answer satisfactorily. To ascertain the effect of a single element is clearly impossible, since it is almost inconceivable that the vibration periods of its valency electrons should be unaffected by the chemical conditions under which the atom is placed. There is, however, a better prospect of detecting the absorption of a group of atoms which form a characteristic unit in the molecule, especially if the group contain a labile system of

electrons.   From the occurrence of certain bands, it has been found possible to infer the presence of the dynamic conditions set up by enol-keto tautomerism,[1] by the dicarbonyl group,[2] or by the benzene system.[3]   These examples are merely special cases of the general rule established by Hartley, that substances of closely allied structures have absorption curves of similar shape.   This, perhaps, is the most useful generalization made from the relations between absorption and constitution, and, as we shall presently see, it has been employed with great success in determining the constitution of substances.

Spring has claimed[4] that additive relations can be detected in the very weak selective absorption which is exerted in the visible spectrum by some aliphatic compounds.   According to Spring, the number of bands in this spectrum is controlled by the number of hydrocarbon groups in the molecule.   The esters of fatty acids contain two hydrocarbon nuclei, and so give two absorption bands, each of which corresponds to the acid and alcoholic radicle.   For example, ethyl acetate shows two bands at 632 and 615 (arbitrary scale), whilst ethyl alcohol alone gives one band at 633, and acetic acid another at 615.

The distinctive feature of absorption in the infra-red spectrum is the predominance of additive relations.   This will be fully illustrated in the section of this chapter dealing with absorption in that region.

We shall now discuss the chief relations which have been observed between chemical constitution and absorption.   The different methods of experiment adopted, and the wide scope of the data, render it difficult to deal with the subject so as to avoid confusion.   The following scheme will be followed as the best that can be devised for our purpose.

A. General absorption.

B. Selective absorption.

(1) Infra-red absorption.

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[1] Baly and Desch, *Trans. Chem. Soc.*, 85, 1029 (1904) ; 87, 766 (1905).

[2] Stewart and Baly, *Trans. Chem. Soc.*, 89, 502 (1906).

[3] Baly, Edwards and Stewart, *Trans. Chem. Soc.*, 89, 544 (1906).

[4] Spring, *Rec. Pays. Bas.*, 16, 1 (1897).

(2) Visible and ultra-violet absorption.

    (*a*) Colour; (*b*) absorption and the dynamic state of the molecule; (*c*) influence of substitution on absorption.

(3) Application of absorption spectra to determining chemical constitution.

A. General Absorption

§ 5. *GENERAL ABSORPTION AND CONSTITUTION*

In an address to the chemical section of the British Association,[1] Hartley discussed the relations between the type of ultra-violet absorption and the structure of compounds. He observed that all compounds which exert selective absorption are of aromatic character, such as benzene, pyridine, pyrazine, and their derivatives.[2] Those exerting strong general absorption possess a cyclic structure like the foregoing class of compounds, but they lack the true aromatic character. Examples of this class are: furfurane,[3] thiophene,[3] pyrrol,[3] piperidine,[4] dihydrobenzene,[5] cineol,[5] and many other terpenes. On the other hand, compounds which possess merely a weak general absorption are built up of an open chain of atoms, such as the fatty alcohols,[6] acids,[6] esters,[6] nitrates,[8] and amines,[6] olefines,[9] acetylene,[9] hydrocyanic acid,[10] and the polyhydric alcohols.[7] The absorption shown by the latter class of compound is readily distinguished from that of the cyclic bodies; since, as a rule,

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[1] Report of the British Association, 1903.

[2] Hartley and Dobbie, *Trans. Chem. Soc.*, **73**, 695 (1898); **77**, 846 (1900).

[3] *Trans. Chem. Soc.*, **77**, 846 (1900).

[4] *Phil. Trans.*, 471 (1885).

[5] Hartley and Huntington, *Proc. Roy. Soc.*, **1** (1881).

[6] Hartley and Huntington, *Phil. Trans.*, **170**, 257 (1879).

[7] Hartley, *Trans. Chem. Soc.*, **51**, 58 (1887).

[8] Soret and Rilliet, *Comptes Rend.*, **89**, 747 (1879); Hartley, *Trans. Chem. Soc.*, **81**, 556 (1902).

[9] Hartley, *Trans. Chem. Soc.*, **39** (1881).

[10] Hartley, *Trans. Chem. Soc.*, **41**, 45 (1882).

it appears only at the more refrangible end of the spectrum, and rapidly weakens as the number of molecules in the path of the light is lessened.

Recent observations have shown that this classification is not strictly correct, for it has been found that many open chain ketones containing the —CH_2—CO—[1] or —CO—CO—[2] grouping exert selective absorption at the visible end of the violet region. However, it should be observed that the selective absorption of these exceptional cases usually is not so intense as that of true aromatic compounds. With regard to general absorbents, the classification still holds good, and it may be said that general absorption indicates the presence of ordinary cyclic structure, or of the open-chain type. It might be argued that the few nitro derivatives of benzene which have intense general absorption,[3] are exceptions to the rule; but it seems that in these compounds the nucleus has lost the true aromatic character.

By comparing the spectra of the various compounds mentioned above, it may be shown that the increase of carbon atoms in a homologous series causes the general absorption to increase, and to extend towards the red. The replacement of hydrogen by hydroxyl, carboxyl, and other oxygen complexes, has no effect on the general character of the spectrum, but merely augments the absorptive power. Unsaturation[4] has the effect of greatly increasing the general absorption of fatty alcohols and acids. Stewart has also observed[5] that the molecular rotations of the amyl esters of the unsaturated and saturated acids stand in the same relative order as the general absorptive powers of the acids themselves. The absorption curves of maleic, fumaric, and succinic acids are illustrated in the accompanying figure.

[1] Baly and Desch, *Trans. Chem. Soc.*, **85**, 1029 (1904) ; **87**, 766 (1905) ; Stewart and Baly, *Trans. Chem. Soc.*, **89**, 489 (1906).

[2] Baly and Stewart, *Trans. Chem. Soc.*, **89**, 503 (1906).

[3] Baly and Collie, *Trans. Chem. Soc.*, **87**, 1344 (1905) ; Baly, Edwards and Stewart, *Trans. Chem. Soc.*, **89**, 516 (1906).

[4] Magini, *Atti. R. Accad. dei Lincei Roma*, [5] **12**, II., 35 (1904) ; Stewart, *Trans. Chem. Soc.*, **91**, 199 (1907).

[5] Stewart, *loc. cit.*

The rotatory powers of the amyl esters of these acids may also be added,

Diamyl succinate . . $[M]_d = + \ 9\cdot71$
Diamyl maleate . . . $[M]_d = +11\cdot82$
Diamyl fumarate . . $[M]_d = +15\cdot17$

and it is evident that the three esters fall into the same order as the acids when arranged in order of increasing general absorption.
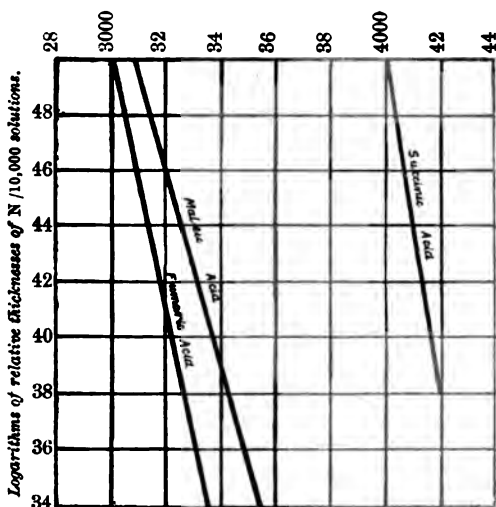
FIG. 12.

Stereoisomerides.—The same curves serve to illustrate the fact that the general absorptive power of ethylenic isomerides [1] is different. Maleic, fumaric, mesaconic, and citraconic acids seem to be the only substances of this type which have been examined, but in each pair the anti-isomeride has the greater absorption.

Although we are here dealing with general absorption, it

[1] Magini, *Journ. de Chim. Phys.*, **2**, 403 (1904) ; Stewart, *Trans. Chem. Soc.*, **91**, 199, 1537 (1907).

should be observed that Hartley has shown that the selective absorption of the two isomeric benzaldoximes is identical.[1] Optical antipodes have the same absorptive power; but in concentrated solutions *dextro* tartaric acid is a weaker absorbent than the racemic acid, and this in turn has a weaker effect than the *meso* compound.[2] Dobbie and Lauder found[3] that the absorption curves of the inactive and *dextro* corydalines, and of tetrahydroberberine and canadine, are identical; but it should be observed that the solutions, in which these isomerides were compared, were more dilute than those employed in the case of racemic and tartaric acids.   In dilute solution the latter compounds exert the same effect, no doubt owing to the breaking up of the racemic complex.   Also it has been found[4] that the externally and internally compensated forms of dibenzoyl succinic ester

$$C_6H_5CO \, . \, CH \, . \, COOEt$$
$$|$$
$$C_6H_5CO \, . \, CH \, . \, COOEt$$

Dibenzoyl succinic ester.
γ isomeride, m.p. 75°.   β isomeride, m.p. 128°.

have identical curves of absorption.

Spring has examined[5] the absorption in the visible region exerted by a number of aliphatic compounds, which under ordinary conditions appear colourless.   With these compounds it seems that the type of visible absorption spectrum is connected with the symmetry of the molecule.   All compounds in which the substituting groups are placed symmetrically with regard to the main carbon chain show general absorption; but if the substituents are collected at one end of the chain, a selective absorption spectrum is shown.

[1] Hartley and Dobbie, *Trans. Chem. Soc.*, **77**, 509 (1900).

[2] Stewart, *Trans. Chem. Soc.*, **91**, 1540 (1907); and Byk, *Zeit. Phys. Chem.*, **59**, 682 (1904).

[3] *Trans. Chem. Soc.*, **83**, 613 (1903).

[4] Hartley and Dobbie, *Trans. Chem. Soc.*, **77**, 498 (1900).

[5] *Rec. Pays. Bas.*, **16**, 1 (1897).

B. Selective Absorption

§ 6.—I. *ABSORPTION IN THE INFRA-RED REGION*

The relations between constitution and absorption in this region of the spectrum [1] have not yet been thoroughly explored, but the data which have been accumulated are sufficient to show that further research will be profitable. Coblentz appears to have begun a systematic study of the infra-red absorption of organic compounds.

In the present state of affairs we cannot proceed further than to illustrate the additive nature of absorption in this region. This characteristic was evident from the earliest results obtained. Abney, using the photographic method, examined simple substances of different chemical nature, such as hydrochloric acid, chloroform, cyanogen, and water, and it was found that when hydrogen is present, a certain group of absorption lines occurs regularly in the same position, and these vanish when this element is removed. Abney therefore ascribed these absorption lines to hydrogen. Inspection of the table given below will show that the alkyl halides have four constant absorption bands between 1 and $1 \cdot 1 \mu$, and since variation of the halogen has no effect on the form or position of the spectrum, these bands must be ascribed to the carbon nucleus.

Also the derivatives of benzene, which in the ultra-violet and visible spectrum have different absorption curves, show a striking similarity in their infra-red absorption. The chemical nature of the derivative seems to have no effect on the band at $8 \cdot 5 \mu$.

Other measurements in this region of the spectrum have

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[1] Abney, *Phil. Mag.*, [5] **7**, 316 (1879) ; *Proc. Roy. Soc.*, **31**, 416 ; **32**, 483 (1881) ; *Phil. Trans.*, **171** (1881) ; Abney and Festing, *Phil. Trans.*, **172**, 887 (1882) ; Julius, *Maandblad vor Natuurwetenschappen*, 6 (1893) ; Puccianti, *Il Nuovo Cim.*, **11**, 241 (1900) ; Angström, *Wied. Ann.*, **58**, 609 (1896) ; Donath, *Wied. Ann. Beiblätter*, **17**, 332 (1882) ; Ilklé, *Phys. Zeit.*, **5**, 271 (1904) ; Coblentz, *Astrophys. Journ.*, **20**, 207 (1904) ; Ransohoff, *Dissertation*, Berlin (1896).

TABLE I.

Substance.	Formula.	Approximate position of the most prominent absorption bands and lines.						
Benzene	C₆H₆	0·71μ	0·855–0·865μ	0·987μ	1·005μ	1·02μ	1·05μ	1·075–1·85μ
Bromobenzene	C₆H₅Br	0·71μ	0·855–0·865μ	0·985μ	1·005μ	1·02μ	1·05μ	1·075–1·85μ
Benzyl chloride	C₆H₅CH₂Cl	0·71μ	0·855–0·865μ	0·985μ	1·005μ	1·02μ	1·05μ	1·075–1·85μ
Aniline	C₆H₅NH₂	0·715–0·72μ	0·855–0·865μ	—	—	—	—	—
Dimethyl aniline	C₆H₅N(CH₃)₂	—	0·855–0·865μ	—	—	1·02μ	—	—
Nitrobenzene	C₆H₅NO₂	0·71μ	0·845–0·855μ	—	1·005μ	—	—	—
Methyl alcohol	CH₃OH	—	—	—	0·96μ	general absorption		
Ethyl alcohol	C₂H₅OH	—	—	—	0·96μ	1·023μ	1·072μ	{ general absorption
Propyl alcohol	C₃H₇OH	—	—	—	0·96μ	1·023μ	1·072μ	1·10μ
Isopropyl alcohol	C₃H₇OH	—	—	—	0·96μ	1·023μ	1·072μ	general absorption
Tert. butyl alcohol	C₄H₉OH	0·9μ	0·91–0·92μ	0·93–0·94μ	0·96μ	1·023μ	1·072μ	1·10μ
Isobutyl alcohol	C₄H₉OH	0·9μ	0·91–0·92μ	0·93–0·94μ	0·96μ	general absorption		
Amyl alcohol	C₅H₁₁OH	0·9μ	—	—	—	1·023μ	1·072μ	1·10μ
Ether	(C₂H₅)₂O	1·02μ	—	—	—	1·026μ	1·072μ	1·10μ
Methyl iodide	CH₃I	1·02μ	1·04μ	1·075μ	1·1μ	—	—	—
Ethyl iodide	C₂H₅I	1·02μ	1·04μ	1·075μ	1·1μ	—	—	—
Propyl iodide	C₃H₇I	1·02μ	1·04μ	1·075μ	1·1μ	—	—	—
Amyl iodide	C₄H₁₁I	1·02μ	1·04μ	1·075μ	1·1μ	—	—	—
Hexyl iodide	C₆H₁₃I	1·02μ	1·04μ	1·075μ	1·1μ	—	—	—
Ethyl bromide	C₂H₅Br	1·02μ	1·04μ	1·075μ	1·1μ	—	—	—
Amyl bromide	C₅H₁₁Br	1·02μ	1·04μ	1·075μ	1·1μ	—	—	—

been carried out with rays of greater wave length, the bolo-meter being employed.

The behaviour of isomeric substances has been discussed by Coblentz, who concludes that isomerides of widely different chemical structure have different absorption curves, whilst those of similar structure, *e.g.* caproic and isocaproic acids, have similar absorption spectra. The constitutive side of the property is here evident.

We may now turn to the absorption exerted by particular atomic groupings. Puccianti, Donath, and Coblentz agree that a narrow absorption band occurring at 1.71μ is due to the grouping C—H, for it occurs in all compounds containing this structure, and is absent from those which do not. Some of the data obtained by Puccianti in support of this conclusion are quoted in the following table.

TABLE II.

Substance.	Formula.	Positions of principal absorption bands and lines.		
Methyl alcohol . .	CH_3OH .	1.71μ	$2.27-2.58\mu$	$2.72-2.75\mu$
Ethyl alcohol . .	C_2H_5OH .	1.71	$2.32-2.55$	$2.69-2.75\mu$
Allyl alcohol . .	C_3H_5OH .	1.71	$2.25-2.58$	—
Methyl iodide . .	CH_3I . .	1.71	$2.27-2.36$	2.58
Ethyl iodide . .	C_2H_5I . .	1.71	$2.29-2.36$	$2.38-2.42$
Ethyl ether . . .	$(C_2H_5)_2O$.	$1.69-1.71$	$2.32-2.55$	—
Benzene	C_6H_6 . .	1.71	2.16	$2.49-2.51$
Toluene	$C_6H_5 \cdot CH_3$	$1.69-1.71$	—	$2.49-2.51$
Ethyl benzene . .	$C_6H_5 \cdot C_2H_5$	1.69	—	$2.49-2.53$
o Xylene	$C_6H_4(CH_3)_2$	1.71	$2.32-2.40$	2.62
m Xylene . . .	,,	1.71	$2.32-2.36$	2.51
p Xylene	,,	1.71	$2.32-2.38$	$2.49-2.51$
Pyridine	C_5H_5N .	$1.69-1.71$	21.8	$2.45-2.51$
Carbon disulphide .	CS_2 . .	—	Transparent	—
Carbon tetrachloride	CCl_4 . .	—	Transparent	—

Ransohoff, investigating the alcohols and glycols, found that the hydroxyl group is responsible for a double band at 3 and 3.4μ; but it may be observed that the band at 3.4μ occurs in hydrocarbons, *e.g.* butane, octane, and mesitylene.

Homologues.—The question as to the effect of additional methylene groups in homologous series has been thoroughly

investigated by Coblentz. In a few series the most careful measurements show that with increasing molecular weight a slight shift takes place towards the spectrum of greater wave length; but inspection of the annexed table will show that this effect, even if it is real and not due to experimental error, vanishes in the derivatives of high molecular weight. It may be recalled that the same behaviour of the effect of homology has been found with selective absorption in the ultra-violet.

TABLE III.

Substance.	Formula.	Maximum absorption band at
Benzene	C_6H_6	$3\cdot25\mu$
Toluene	$C_6H_5CH_3$ . .	$3\cdot3\ \mu$
Xylene	$C_6H_4(CH_3)_2$ . .	$3\cdot38\mu$
Mesitylene	$C_6H_3(CH_3)_3$ . .	$3\cdot4\ \mu$
Propyl alcohol . . .	C_3H_7OH . . .	$1\cdot71, 3, 3\cdot43, 6\cdot06\mu$
Myricyl alcohol . . .	$C_{30}H_{61}OH$ . .	$1\cdot71, 2\cdot95, 3\cdot43, 5\cdot9\mu$
Methane	CH_4	$3\cdot31, 7\cdot70\mu$
Ethane	C_2H_6	$3\cdot39, 6\cdot85\mu$
Butane	C_4H_{10}	$3\cdot42, 6\cdot85\mu$
Octane	C_8H_{18}	$3\cdot4, 6\cdot9\mu$
Tetracosane	$C_{24}H_{50}$ . . .	$3\cdot4, 6\cdot9\mu$

Water of Crystallization and of Constitution.—Coblentz [1] has extended the study of infra-red absorption and emission spectra to minerals with a view to distinguishing between water of constitution and crystallization in these substances. In contrast to its behaviour in the ultra-violet and visible regions, in the infra-red water exhibits a strong and characteristic selective absorption.[2] The chief bands lie in the following positions—

$$1\cdot5\mu, \quad 2\mu, \quad 3\mu, \quad 4\cdot75\mu, \quad 6\mu$$

those at 3μ and 6μ being the strongest of the series. Coblentz finds that those minerals which are known from their chemical behaviour to contain water of crystallization, show spectra in

[1] *Phys. Review*, **20**, 252 (1905); **22**, 1 (1905); **23**, 125 (1906); also Königsberger, *Wied. Ann.*, **61**, 703 (1897).

[2] Julius, *Akad.* Amsterdam, 1 (1892); Paschen, *Wied. Ann.*, **53**, 334 (1894); Aschkinass, *Wied. Ann.*, **55**, 406 (1895).

which these water bands are well developed. On the other hand, anhydrous minerals and those which contain water of constitution present merely as hydroxyl groups, as in bauxite $Al_2O(OH)_4$, do not exhibit any of these bands. The contrast between anhydrite and selenite and between quartz and opal serve to show the influence of free water in a mineral.

		Absorption bands at	
Anhydrite	$CaSO_4$	3·2, 5·7, 6·15, and 6·55μ	small
Selenite	$CaSO_4 \cdot 2H_2O$	1·5, 2, 3, 4·75 and 6μ	strong
Quartz	SiO_2	2·9 and 4·35μ	small
Opal	$SiO_2 nH_2O$	1·5, 2, 3, and 6μ	strong

The bands of quartz and anhydrite are weak in comparison to the well-developed water band of the hydrated minerals. More complete illustration is afforded by the examples quoted in the following list. The first division consists of compounds which do not show the characteristic bands of water ; those containing hydroxyl show a weak band at about 3μ, which Coblentz supposes to be due to this group, since it also occurs in the alcohols. The compounds in the second division exhibit the bands of water, and, with the curious exception of cane sugar, all are known to contain water of crystallization.

TABLE IV.

COMPOUNDS SHOWING NO WATER BANDS.

Substance.	Formula.	Substance.	Formula.
Brucite . . .	$Mg(OH)_2$	Diaspase . .	$AlO \cdot OH$
Gothite . . .	$FeO \cdot OH$	Diatolite . .	$Ca(B \cdot OH)SiO_4$
Manganite . .	$MnO \cdot OH$	Portland cement	—
Bauxite . . .	$Al_2O(OH)_4$	Tourmaline .	—
Lazulite . . .	$MnFeAl_5(OH)_2(PO_4)_2$	Fructose . .	$C_6H_7O(OH)_5$

COMPOUNDS SHOWING WATER BANDS.

Heulandite . .	$H_4CaAl_2Si_6O_{18} \cdot 3H_2O$	Cane sugar . .	$C_{12}H_{12}O_{11}$
Potassium alum.	$K_2 \cdot SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Calcium chloride	$CaCl_2 + 6H_2O$
Potassium ferro-cyanide . .	$K_4Fe(CN)_6 \cdot 3H_2O$	Mellite . . .	$Al_2C_{12}O_{12} \cdot 18H_2O$
		Stilbite . . .	$CaAl_2Si_6O_{16} \cdot 6H_2O$

These relations may be applied to determining the nature of the supplementary molecules of water in a mineral. Thus talc, $H_2Mg_3Si_4O_{12}$, loses water at red heat; but, since the mineral does not show the water bands, the water which is thus expelled must be of constitution. The substance is therefore a basic silicate. Serpentine, $H_4(MgFe)_3SiO_9$, another mineral which loses water at a red heat, shows the strong absorption band of water at 3μ, and therefore contains this substance in the free condition. The application of infra-red absorption to chemical problems is very limited; in fact, these are the only examples.

B.—2. Visible and Ultra-Violet Absorption

(a) *Colour and Chemical Constitution*

§ 7. *THE NATURE OF COLOUR*

The necessity for dealing with absorption in the visible region of the spectrum separately from that in the ultra-violet, arises from the fact that very many chemists have investigated the relations between constitution and the physiological effect of absorption as revealed by the eye. As may well be imagined, with such a ready instrument at the disposal of every chemist, the subject has developed enormously; moreover, the nature of the data, being different to those afforded by the spectrograph, renders expedient a division of the subject. But, as we shall presently see, observations of colour may be roughly translated into terms of absorption, and thus a connection established between the two classes of experimental data. As a preliminary to the study of the relations between colour and chemical structure, we shall briefly discuss the physical nature of this property in its bearing on the present subject.

The total effect of the rays within the visible portion of the spectrum, causes the sensation of white light, but if a portion of these rays be removed, the light appears coloured. The perception of colour depends on the efficiency of the eye

as an instrument for detecting absorption. In the first place, the eye is sensitive only to those rays which are approximately situated between 0.79μ and 0.39μ in the spectrum, and if the absorption occur outside these limits, colour will not appear. Moreover, the appearance of colour depends to a certain degree on the intensity of absorption. There are many substances, such as the fatty alcohols, which appear colourless under ordinary circumstances, even though they absorb rays in the visible part of the spectrum, and it is only when they are examined [1] in layers of considerable thickness that the colour becomes manifest.

We see, then, that as an instrument for detecting absorption, the eye is lacking both in breadth and depth of efficiency, and, although it admirably combines its numerous functions, for the present purpose it is inferior to the spectroscope. The observation of colour does not afford an accurate quantitative measurement of the wave length of the absorbed rays, but often it is possible roughly to interpret colour in terms of absorption. If, for example, a substance appear bright blue, it may be inferred that absorption is exerted in the red or orange region ; if greenish yellow, violet absorption, and so on. [2]

From what has now been said of colour, it is evident that the term is inexact, and it is difficult to say whether substances like alcohol and water should be regarded as coloured or not. As a general rule, it may be said that a coloured substance is one which exerts strong absorption within the ordinary limits of vision. Many chemists seem to have ignored the fact that colour is merely a special case of absorption, whilst others, recognizing this relation, have set different meanings to the term. From the confusion which has thus arisen, it may seem unfortunate that the influence of constitution on colour, instead of absorption, ever was studied; but many of the more important relations known between constitution and absorption were first approached from the standpoint of colour.

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[1] Spring, *Proc. Soc. Roy. de Belg.*, 246 (1896) ; 165 (1897).

[2] For further information on this subject the reader should consult a text-book of physics, or, for details, Helmholtz's *Physiologische Optik*.

§ 8. *THE RELATIONS OBSERVED BETWEEN COLOUR AND CONSTITUTION*

The relations between colour and molecular structure were first discussed[1] in 1867 by Graebe and Liebermann, who studied the effect of reducing coloured organic compounds. Since quinone, rosaniline, indigo, azobenzene and other coloured bodies are converted by nascent hydrogen into colourless compounds, it was inferred that all coloured compounds contain elements in the unsaturated condition. Considering the undeveloped state of structural chemistry at that time, it is scarcely surprising that Graebe and Liebermann were unable to proceed further than this rough generalization. It was not until ten years later, when the constitution of many of the dye-stuffs had been elucidated, that Witt was enabled to point out[2] some general relations between the structure, colour and dyeing properties of organic substances.

Chromophores.—By comparing the structures of colourless bodies with those of coloured derivatives, it is evident that the colour of the latter is conditioned by the presence of certain groups. Witt applied the term "chromophore" to these colour-exciting groups, and the following list shows some of the more important examples.[3]

$>$C—CO—CO—C$<$
a Dicarbonyl group.
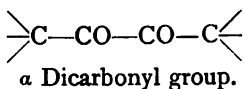
Occurring in diacetyl, benzil, cro-conic acid, phenanthrenequinone, etc.

$>$C—NO$_2$
Nitro group.
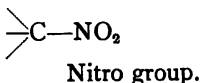
In aromatic nitro-compounds, nitro-benzene, and nitronaphthalene.

$>$C—NO
Nitroso group.
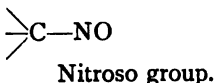
In aromatic and some aliphatic nitroso compounds.

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[1] *Ber.*, **1**, 106 (1867).

[2] *Ber.*, **9**, 522 (1876).

[3] For further illustration, Nietzki, *Chemie der Organ. Farbstoffe*, Berlin, p. 6, 1901 ; *Ueber den Zusammenhang zwischen Farbe und Konstitution*, Kauffmann, Stuttgart, p. 7, 1904.

$\equiv$C—N$=$N—C$\equiv$
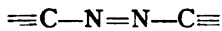
Azo group.

In aromatic and aliphatic azo derivatives, *e.g.* azobenzene and azoformic acid.
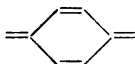
p Quinonoid group.

In quinone, anthraquinone, indophenols, indamines, and many dye-stuffs.

o Quinonoid group.

In ortho-quinone, safranine, oxazines, thiazines, pyronines, and other classes of dye-stuffs.
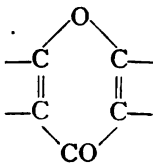
In the flavone and xanthone dyes.

γ Pyrone group.

Witt drew attention to the fact that by no means all coloured compounds are endowed with dyeing properties, and he showed that a substance does not become a dye until a salt-forming group is inserted in addition to the chromophore. Thus azobenzene $C_6H_5N=NC_6H_5$, which contains the chromophoric azo group, is merely coloured; but if hydroxyl or amino groups are introduced, dyes are formed, such as Manchester brown $NH_2 . C_6H_4 . N=NC_6H_3(NH_2)_2$, chrysoidine $C_6H_5N=NC_6H_3(NH_2)_2$, and oxyazobenzene. Similarly, nitrophenol and nitroaniline behave as dye-stuffs in distinction to nitrobenzene, which is weakly coloured. Substances which contain merely the chromophore without the salt-forming group have been termed *chromogens.*

The ideas entertained by Witt on this question may be summed up as follows :—

1. The dyeing properties of aromatic compounds are conditioned by the presence of both a chromophore and a salt-forming group.

2. A chromophore exerts its colour-producing influence to

a greater extent in the salts of the dyes than in the free substances. For example, the colours of alizarine and picric acid are not so intense as those of their salts.

3. If two dyes are of similar constitution, that which forms the more stable salts has the strongest dyeing properties.

Auxochromes.—Somewhat later, Witt observed that many of these salt-forming groups which convert the chromogen into a dye-stuff also strengthen the colour of the substance, and he therefore suggested [1] that such groups should be termed auxochromes. The carboxylic and sulphonic acids derived from azobenzene

$$C_6H_5N=NC_6H_4SO_3H \quad C_6H_5N=NC_6H_4COOH$$

are capable of behaving as dye-stuffs; but the salt-forming groups, carboxyl and sulphonyl, are not auxochromes, since the colour of the derivatives is very similar to that of azobenzene. On the other hand, oxyazobenzene and aminoazobenzene

$$C_6H_5—N=NC_6H_4 . OH \quad C_6H_5N=NC_6H_4NH_2$$
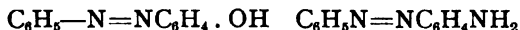
are more intensely coloured than the chromogen, and here the hydroxyl and amino groups function as auxochromes.

Generally speaking, the auxochromes are unsaturated, the best examples being the hydroxyl, amino, and dimethylamino groups. The theory of the action of the auxochromes has been recently studied by Kauffmann in connection with luminescence and fluorescence.[2] Kauffmann finds that the insertion of an auxochrome into the benzene nucleus tends to excite not only colour but also a number of other phenomena, such as luminescence, optical anomaly, and magneto-optical anomaly, all of which run parallel to one another. This peculiar property of the auxochromes is said to be due to the influence exerted by their residual affinities on that of the benzene nucleus. In benzene, or any of its derivatives which contain saturated substituents, the free affinities of the nuclear carbon atoms are in a state of

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[1] *Ber.*, **21**, 325 (1894).

[2] For fuller details the reader is referred to the chapter dealing with this subject.

equilibrium; but as soon as the unsaturated auxochrome is introduced the balance is upset, and these anomalies appear. When a quantitative measure of the anomaly can be obtained, it is found that the magnitude roughly corresponds to the degree of unsaturation of the different auxochromes.[1]

It is important to observe that, besides these changes in the physical properties of the substance, the chemical nature of both the benzene system and the auxochrome undergo a transformation. Thus on passing from benzene to aniline we arrive at a substance which is optically abnormal, and is luminescent under the influence of the Tesla discharge; at the same time the chemical properties of the amino group and the benzene nucleus alter, the latter being now more reactive. Aniline, however, is not coloured, but this seems merely due to the fact that the new absorption band introduced does not lie in the visible region.

There is no doubt that the colour of a substance is influenced by the position occupied by the auxochrome. In many groups of compounds it has been observed that a particular position of the auxochrome is favourable to the appearance of colour, whilst in the same positions the auxochrome appears to be inactive. For illustration of this effect we may turn to the large class of natural dye-stuffs derived from benzo-γ pyrone. In the hydroxyl derivatives of this group it seems that there are three positions of the substituent favourable to colour. In the first place the *peri* position of hydroxyl with respect to carbonyl is favourable, as may be seen from the comparison of oxyxanthones.

1. Oxyxanthone.   2. Oxyxanthone.   3. Oxyxanthone.
   Yellow.   Weak yellow.   Colourless.

4. Oxyxanthone is also colourless.
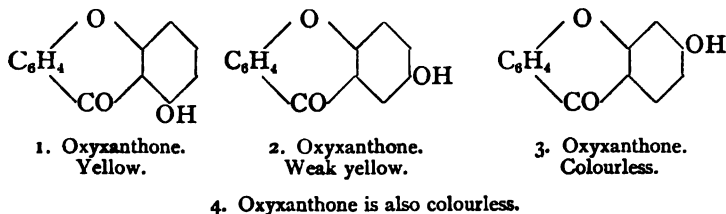
[1] A complete account of Kauffmann's views of the action of auxochromes will be found in *Die Auxochrome*, H. Kauffmann, Stuttgart, 1907.

But this arrangement of hydroxyl is not the most active, for the more intensely coloured derivatives of flavone contain two hydroxyl groups in the ortho position with respect to one another. Thus luteoline is more strongly coloured than apigenine.
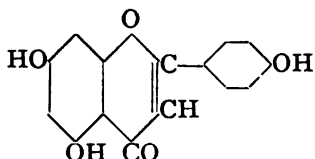
Apigenine.
Pale yellow in alkali.
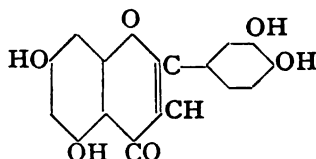
Luteoline.
Deep yellow in alkalies.

It may be remarked that this rule holds also with the hydroxyl derivatives of anthraquinone.

Kostanecki has recently shown[1] that perhaps the most potent factor in determining the colour of the flavone dyes is the presence of the $CO—C(OH)=$ grouping. This structure is present in all the more intensely coloured dye-stuffs of the flavone series, and resomorine, which resembles morine and
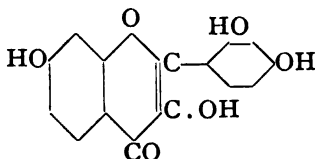
Resomorine.
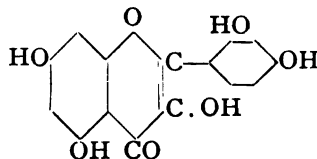
Morine.
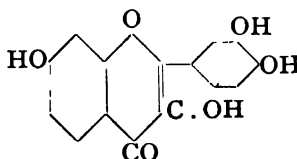
Fisetine.

fisetine in colouring power, does not contain either the ortho-hydroxyl groups or the $HO . C—C—CO—$ arrangement.

[1] Kostanecki, Lampe and Triulzi, *Ber.*, **39**, 92 (1906).

Before leaving this question of substitution and colour, it should be noticed that the mass of the inserted group may be of influence; but the effect is subordinate to that of the chemical nature of the group.

§ 9. *THE QUINONOID STRUCTURE*

The ortho or para quinonoid arrangement has been so frequently observed in the strongly coloured dye-stuffs that some chemists have come to regard the occurrence of colour as showing the presence of this structure in a substance. The structural formulæ advanced for these substances have not always been firmly based on chemical evidence, and much controversy has been raised concerning them. We shall not follow in detail the lengthy discussions which have arisen over the individual types of compounds, but we shall briefly deal with the main points at issue.

Of all those who have at one time or another advocated the quinonoid structure for coloured compounds, Armstrong [1] is the most consistent. He seems at first to have been of the opinion that all coloured benzenoid derivatives contain this structure, and he suggested that the structural formulæ of these compounds should be written accordingly; thus azobenzene and the salts of the nitrophenols would be—
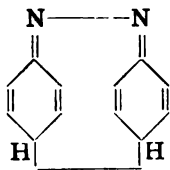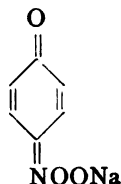
Azobenzene.   Sodium *p* nitrophenate.

[1] Armstrong, *Proc. Chem. Soc.*, 27 (1882) ; 101, 189, 195 (1892) ; 53, 55, 63, 206 (1893) ; 228 (1897) ; 101 (1902) ; also *Encyclopaedia Britannica*, vol. 26, 746 (1902) ; Armstrong and Robertson, *Trans. Chem. Soc.*, 87, 1272 (1905).

Later, however, Armstrong recognized that, to be satisfactory, any theory of the origin of colour in carbon compounds must embrace the simple substances of the aliphatic series, and he therefore recast his views in a more general form. He then assumed that unsaturated atoms or groups may act as "light-absorbing centres," and it is by the "co-operation" of these that colour is produced. In most cases, at least three such centres of absorption must be present to cause a pronounced colour. In the para-quinonoid structure (I.) there are four of these absorption centres—
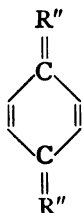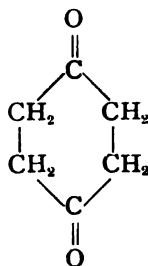
I.   II.

the two unsaturated $>C=R''$ groups and the ethenoid linkages of the cyclic nucleus, and the substance is strongly coloured; but in 1·4 diketo-hexamethylene (II.) there are only two of these groups, and colour is not developed. There are many coloured substances which contain an open chain of atoms, but the unsaturated groups necessary for light absorption are always present. Armstrong terms this class of compound pseudo-quinonoid; perhaps the best examples are—

$$CH_3CO . COCH_3 \qquad CHI_3$$
Diacetyl.   Iodoform.

In diacetyl the carbonyl groups, and in iodoform the iodine atoms, function as light-absorbing centres, and when the number of these is lessened, as in

$$CH_3COCH_2CH_3 \qquad CH_2I_2$$
Methyl ethyl ketone.   Methylene iodide.

the colour vanishes.

The claims made by Armstrong for the quinonoid structure of some of the highly coloured benzene derivatives have in many cases been verified and extended to similar compounds by the later work of other chemists. Hantzsch, in his recent experiments with the nitro-phenols, has found chemical evidence for the existence of the quinonoid structure in the red alkali-salts of these substances. It may be observed that the researches of Hantzsch were not undertaken expressly to show the quinonoid nature of these compounds, but to support his theory that any colour change which takes place on salt-formation is due to change of structure. There are many aliphatic and benzenoid nitro compounds which, although nearly colourless, furnish intensely coloured alkali-salts, such, for example, as the derivatives of dinitromethane (I.) and the mononitrophenols (II.).

$$R . CH(NO_2)_2 \qquad C_6H_4OH . NO_2$$
$$\text{I.} \qquad\qquad\qquad \text{II.}$$
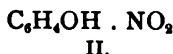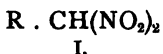
In some cases it is possible to isolate both the coloured and colourless series of salts[1] or the corresponding alkyl derivatives. These coloured isomers have been termed *chromo-isomerides*. With the nitro-phenols the " chromo " series of ethers is difficult to obtain ; they are formed in small amount together with the true phenolic ethers by the action of alkyl halide on the dry silver salt of the phenol. According to Hantzsch the pure compounds of phenolic structure are colourless, and the weak colour of some nitro-phenols, *e.g. o.* nitrophenol, is due to the presence of the " chromo " isomeride in solid solution.

In a few cases, such as these nitro-phenols, the original quinonoid theory of colour, being supported by chemical evidence, has held ground; but there are many coloured substances to which the true quinonoid structure can only be

[1] Hantzsch and Gorke, *Ber.*, **39**, 1073, 1084 (1906) ; Hantzsch, *Ber.*, **39**, 3074 (1906); **40**, 338 (1907) ; Hantzsch, Borchers, Salway and Hedley, *Ber.*, **40**, 1533 (1907) ; Hantzsch and Scholtze, *Ber.*, **40**, 4875 (1907) ; Torrey and Hunter, *Ber.*, **40**, 4332 (1907).

doubtfully applied, and yet others for which it is impossible.[1] For this reason the theory has undergone modification. Many chemists, following the lead of Armstrong, are content to explain the colour of these exceptional compounds by the occurrence of unsaturated groups in positions resembling those taken up in the quinones. The structural resemblance between the derivatives of fulvene and *p*. benzo-quinone is evident from the formulæ—
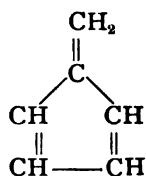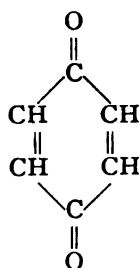
Fulvene.   *p* Benzo-quinone.

Another interesting example of this application of the quinonoid theory is the explanation given by Stobbe[2] for the colour of the fulgides.
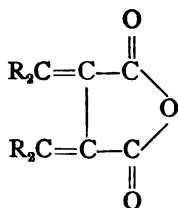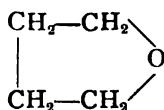
Fulgide.   Tetrahydrofurane.   Tetrahydrobenzene.
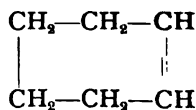
The fulgides are derivatives of tetrahydrofurane, from which they may be derived by replacing the eight hydrogen atoms by four bivalent groups. Tetrahydrofurane corresponds to tetrahydrobenzene, from which ortho and para quinones are

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[1] See Silberrad, *Trans. Chem. Soc.*, **89**, 1793 (1906).

[2] *Ann.*, **349**, 333 (1906).

derived by similar substitution. The fulgides are thus seen to be analogous to the ortho and para benzoquinones.

The impossibility of applying the quinonoid structure to all coloured compounds has been clearly demonstrated by Baeyer and Villiger[1] in their researches on the basic properties of oxygen and carbon. It was found that many colourless or weakly coloured substances which contain these elements in the basic condition furnish strongly coloured salts. The best examples of this " halochromism," as it is called, are found in substances of the type of benzalacetone, and in the simple derivatives of triphenyl methane.

TABLE V.

	Salts.
Dibenzalacetone, pale yellow	orange hydrochloride
$C_6H_5CH=CHCOCH=CHC_6H_5$ . . .	black hydriodide
Dianisylacetone, pale yellow	blue red hydrochloride
$CH_3OC_6H_4CH=CHCOCH=CHC_6H_4OCH_3$	black hydriodide
Trianisylmethane, colourless	
$(C_6H_4OCH_3)_3 : CH$	red sulphate
Trianisyl carbinol, colourless	
$(C_6H_4OCH_3)_3 : C \cdot OH$	red hydrochloride
Tri-p-chlorophenyl carbinol, colourless	
$(C_6H_4Cl)_3 : C \cdot OH$	red sulphate

Kehrmann[2] had previously suggested that the coloured salts of triphenyl carbinol should be represented by the quinonoid structure : *e.g.*—
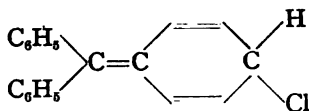
If this view were correct the methoxy and chloro derivatives would be—

[1] *Ber.*, **35**, 1189, 3015 (1902) ; **38**, 569 (1905) ; **40**, 3087 (1907).

[2] *Ber.*, **34**, 3815 (1901); also Norris and Sanders, *Amer. Chem. Journ.*, **25**, 54 (1901).

$(C_6H_4OCH_3)_2 : C=C$
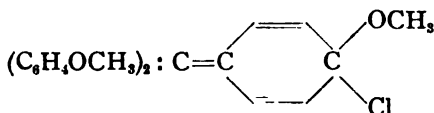
Chloride of trianisyl carbinol.

$(C_6H_4Cl)_2 : C=C$
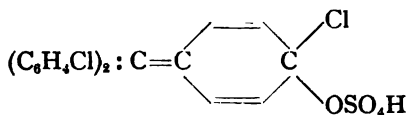
Sulphate of tri-*p*-chlorophenyl carbinol.

According to these formulæ the halogen salts of the methoxyl derivatives should readily liberate methyl halide, and in the sulphate of the tri-*p*-chlorophenyl carbinol one halogen atom should be as reactive as that in triphenyl chloro-methane. Baeyer showed that the substances do not react in this manner, and therefore the quinonoid structure must be discarded.

Moreover, Hantzsch and Leupold[1] have recently found that polymerization may influence the colour of a substance. The halogen acid salts of N methyl phenylacridonium vary in colour from pure yellow to deep brown. It was shown that in the yellow solutions the salts are in the mono-molecular state, whilst in the brown solutions they are trimolecular.
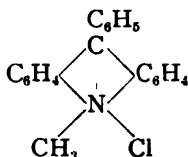
		Chloride.				Iodide.
Solid . . .		Yellow .	.	.	.	Black.
In CHCl$_3$ . .		Yellow .	.	.	.	Brownish black.
In water . .		Yellow green	.	.		Yellow green.

Dilute solutions of the iodide in dissociating media are similar to those of the chloride, since the complex molecules

[1] *Ber.*, **42**, 68 (1909).

are then broken up and the salt is iónized, the colour being due to the acridonium ion.

These exceptional cases are sufficient to show that the quinonoid theory cannot be generally applied to coloured compounds. Moreover, the work of Willstätter [1] and his pupils has raised the fundamental question whether the strongly coloured dye-stuffs, with which the quinonoid theory originated, really possess the true quinonoid structure, and are not instead quinhydrones.

By employing dry silver oxide in ethereal solution as an oxidizing agent, Willstätter succeeded in converting the aromatic amines and aminophenols into the corresponding quinone-imines : *e.g.*—

$$\underset{\text{NH}_2}{\overset{\text{NH}_2}{\bigcirc}} \quad \xrightarrow{\text{O}} \quad \underset{\text{NH}}{\overset{\text{NH}}{\bigcirc}}$$
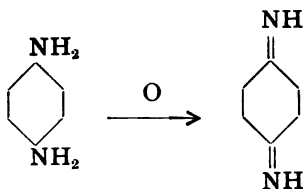
Contrary to expectation, these substances proved to be colourless, or, at most, weakly coloured in solution. For example—

Imino quinone, $O = C_6H_4 = NH$ . . . . colourless.
Methyl iminoquinone, $O = C_6H_4 = NCH_3$ . . . . . pale yellow.
Diiminoquinone, $NH = C_6H_4 = NH$ . . . . colourless.
Methyl diiminoquinone, $NH = C_6H_4 = NCH_3$ . . . . pale yellow.
Sym. dimethyl diiminoquinone, $CH_3 \cdot N = C_6H_4 = NCH_3$. pale yellow.

Several imino compounds of the triphenyl methane series had been previously obtained, and of these the more important are—

$HN = C_6H_4 = C(C_6H_5)(C_6H_4NH_2)$,[2] yellow.   Dye salt : Döbner's violet.
$HN = C_7H_6 = C(C_7H_6NH_2)_2$, orange yellow.   Dye salt : New fuchsine.
$C_2H_5N : C_{10}H_6 : C(C_6H_4)N(CH_3)_2$, orange yellow·   Dye salt : Victoria
blue R.

[1] *Ber.*, **87**, 1494, 3761, 4605 (1904) ; **88**, 2244 (1905) ; **41**, 1458 (1908) ; **42**, 1902 (1909).

[2] Baeyer and Villiger, *Ber.*, **87**, 2848 (1904).

These substances resemble the simpler quinone-imines in the weak colour of their solutions, but with acids they yield the intensely coloured dye-salts, whereas quinonediimine ˙and *asym.* dimethyl di-iminoquinone furnish colourless salts. Now Hantzsch[1] has shown that, as a general rule, a marked change of colour on salt-formation is accompanied by a change in molecular structure, so that it would seem that the dye-salts are of different nature from the true quinonoid imino compounds. In 1879 Würster,[2] by the action of bromine on a solution of *p.* amino dimethylaniline, obtained a red dye-stuff which was later shown by Bernthsen[3] to be of quinonoid character. This substance was supposed to have the empirical formula $C_8H_{11}N_2Br$, and according to Nietzki[4] it should be represented as—

$$(CH_3)_2N \underset{Br}{=} \langle \rangle = NH$$
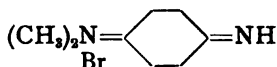
However, Willstätter and Piccard, by oxidizing *p.* amino dimethylaniline in alcoholic solution with nitrous acid succeeded in obtaining the nitrate of this quinone-imine—

$$(CH_3)_2N = \langle \rangle = NH \cdot HNO_3$$
$$\underset{NO_3}{|}$$
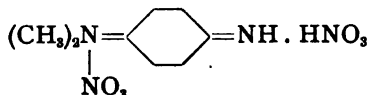
Nitrate of asym. dimethyl diminoquinone.
Colourless.

and it was colourless, thus showing that the accepted structure for Würster's red salt was probably incorrect. Analysis of the red salt showed that the elementary composition corresponds to $C_8H_{12}N_2Br$, and it was then found that this salt is formed as an intermediate product in the oxidation of *p.* amino dimethyl-aniline to the quinone imine. It follows, therefore, that Würster's red is not a pure quinone, and this was confirmed

[1] *Ber.*, **39**, 1084, 3072 (1906).
[2] *Ber.*, **12**, 1803, 1807, 2071 (1879).
[3] *Ann.*, **230**, 162 (1885); **251**, 11, 49, 82 (1889).
[4] *Organische Farbstoffe*, 5th edition, 199 (1906).

by synthesis from the salts of the pure iminoquinone and leuco base. Estimation of the oxidizing power of Würster's red* salt showed that half the molecule is quinonoid. The constitution of the semi-quinonoid molecule is not so easily proved; but since the centre of the strong residual affinity possessed by the quinone-imines is always at the nitrogen atoms, it is reasonable to suppose that in the red dye salt the quinone and leuco base are united by the residual affinities of these atoms. The substance would then be expressed by the formula—

Würster's red.
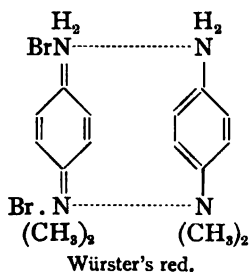
Substances of this partially quinonoid type are called *meri-quinones* in distinction from the colourless salts of the pure imino-quinones which are termed *holo-quinones*. The actual state of affairs in the meri-quinone molecule cannot be correctly shown by the ordinary formula. It is supposed that a dynamic equilibrium is established between the residual affinities of the benzene nuclei present, so that the quinonoid state may be imagined to be equally distributed between them.

These ideas may be directly extended to the triphenyl methane dye-salts. In Würster's red the equilibrium is intermolecular, whereas in dyes such as Döbner's violet it would be intramolecular, being established between two of the benzene systems of the triphenyl-methane nucleus. We shall shortly have occasion to return to this theory of the origin of colour in the triphenyl-methane dye-stuffs, but at present we need only observe that the facts discovered by Willstätter throw grave doubts on the fundamental assumption of the quinonoid theory. With advancing research the weaknesses of

this theory have become more and more apparent, and the same may be said of the chromophore theory in general. We have seen that the appearance of colour depends on the presence of an absorption band of at least moderate intensity in the visible spectrum. It is therefore clear that chromophores are merely groups of atoms containing a peculiarly mobile system of particles whose periods of vibration happen to lie in this visible region. The limited scope of the chromophore theory is further shown by the existence of compounds which are colourless, although they contain one of the recognized chromophoric groups. Such bodies are usually simple derivatives of the chromophore, and the absence of colour is due to the occurrence of the absorption in the ultraviolet region of the spectrum instead of in the visible. When suitable groups are inserted the vibration periods of the chromophore may be brought within the range of the eye. It is unnecessary here to discuss in detail the influence of substitution on absorption ; but it may be observed that, in general, the absorption of the parent substance is shifted towards the red region. The same may be said of increasing molecular complexity, as may be seen in the following series :—

$$\begin{array}{cc} C_6H_5 \diagdown & \diagup C_6H_5 \\ & C{-}C \\ C_6H_5 \diagup & \diagdown C_6H_5 \end{array} \qquad \begin{array}{cc} C_6H_4 \diagdown & \diagup C_6H_5 \\ \big| & C{=}C \\ C_6H_4 \diagup & \diagdown C_6H_5 \end{array}$$

Tetraphenyl ethylene.   Diphenylene diphenyl ethylene.
Colourless.   Colourless solid, yellow solutions.

$$\begin{array}{cc} C_6H_4 \diagdown & \diagup C_6H_4 \\ \big| & C{=}C \big| \\ C_6H_4 \diagup & \diagdown C_6H_4 \end{array}$$

Bisdiphenylene ethylene.
Red, solid.

or—
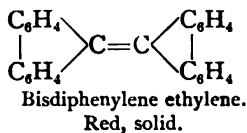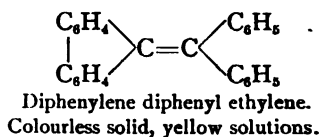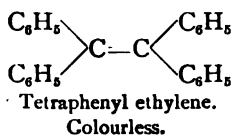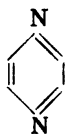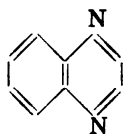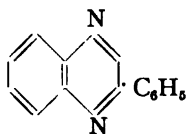
Pyrazine.   Quinoxaline.   Phenyl quinoxaline.   Diphenyl
Colourless.   Colourless.   Pale yellow.   quinoxaline.
                                                  Bright yellow.

Bearing in mind this effect of substitution we might regard as chromophores all groups which exert characteristic absorption, those of visible vibration period being "actual" and those of ultra-violet period being "potential" chromophores. Even in this expanded form the chromophore theory does no more than afford a method of classifying coloured substances. To advance beyond this limit the cause of absorption must be discovered, and then the relations between this and the chemical structure of the absorbent group may be shown.

In the introductory portion of this chapter we saw that Hartley has shown that absorption is caused by the vibrations of intramolecular particles synchronizing with those of the incident light waves; and from the work of Drude it is evident that these vibrating particles are sub-atomic and probably correspond to the valency electrons. Therefore the relations between absorption and constitution must be sought in the dynamic condition of the valencies of the absorbing group.

In the next chapter we shall discuss the chief groups in which the relation between absorption and this dynamic condition has been detected.

CHAPTER XI

B.—2. Absorption in the Visible and Ultra-Violet Regions—*continued.*

(b) *Absorption and the Dynamic Condition of the Molecule*

§ 10. *THE KETO-METHYLENE GROUP:* —CH$_2$—CO—

On examining the ultra-violet absorption spectra of substances containing this group, Baly and Desch[1] observed that whilst all the metallic salts exert well-defined selective absorption in this region, many of the parent compounds show merely general absorption.

TABLE VI.

Substance.	Absorption.	Salts.	Absorption.
Acetonyl acetone CH$_3$COCH$_2$CH$_2$COCH$_3$	general	—	—
Acetoacetic ester CH$_3$COCH$_2$COOC$_2$H$_5$	general	Na and Al	selective
Ethyl acetoacetic ester CH$_3$COCH(C$_2$H$_5$)COOC$_2$H$_5$ . . .	general	—	—
Oxaloacetic ester (COOC$_2$H$_5$)COCH$_2$(COOC$_2$H$_5$) . .	general	Na	selective
Acetone dicarboxylic ester (COOC$_2$H$_5$)CH$_2$COCH$_2$COOC$_2$H$_5$.	general	Na	selective
Acetyl succinic ester (COOC$_2$H$_5$)CH(COCH$_3$)CH$_2$COOC$_2$H$_5$	general	Na	selective
Acetyl acetone CH$_2$COCH$_2$COCH$_3$	selective	Na, Be, Al, Th	selective

[1] *Trans. Chem. Soc.*, **85**, 1029 (1904) ; **87**, 766 (1905).

Now the absorption curves of acetyl acetone and its
metallic derivatives (see Fig. 13) are so similar that it is clear

1 = acetyl acetone.
2, 3, 4 = Be, Al, Th salts, respectively.
5 = methyl acetyl acetone.
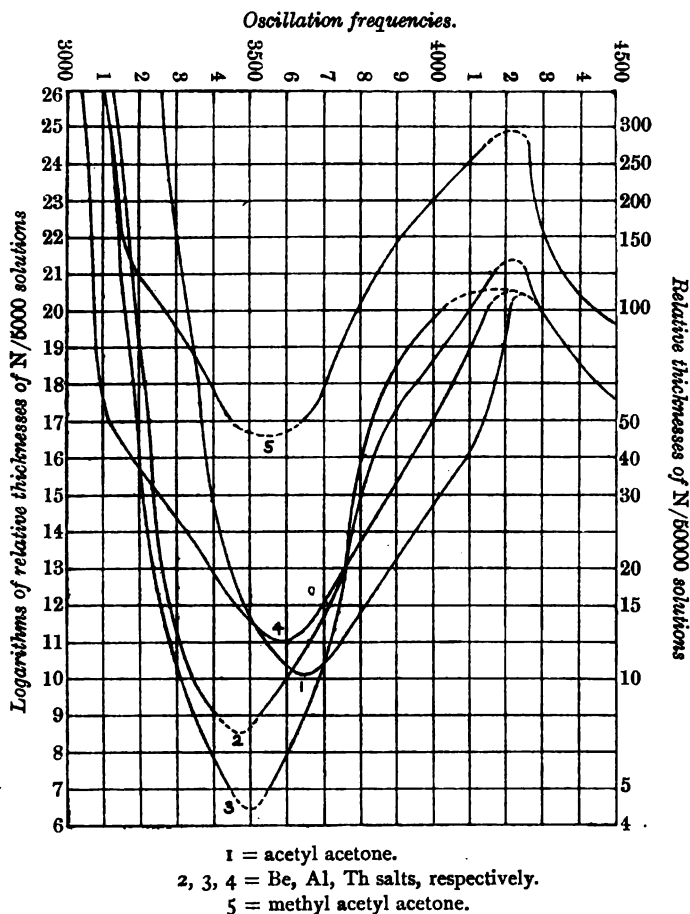
FIG. 13.

that the metallic salts and the parent substance have the same
structure; and since it is generally accepted that the former
have the enolic structure, it might be supposed that the

selective absorption is merely due to the enolic compounds. This view seems to be confirmed by the case of acetyl acetone, which from measurements of refractive power and magnetic rotation appears to contain a large proportion of the enolic isomeride. Thus ethyl acetoacetate and the other esters which give only general absorption would be purely ketonic.

These conclusions, however, are at variance with the results obtained by Hartley, who has examined many fatty alcohols and ethylenic compounds, but has never met with selective absorption in substances of these types. In order to put the question to the test, Baly and Desch turned to the oxygen-ethyl derivatives of the enolic compounds :

$$CH_3 \, C{=}CHCOOC_2H_5 \qquad\qquad H_5C_2OOC \cdot C{=}CHCOOC_2H_5$$
$$\underset{OC_2H_5}{|} \qquad\qquad\qquad\qquad\qquad \underset{OC_2H_5}{|}$$
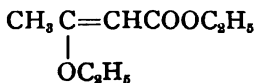
β Ethoxy crotonic ester.   Ethoxy fumaric ester.
General absorption.   General absorption.

and since only general absorption was found, they were forced to conclude that the selective effect is not due to the enolic structure. Further, it cannot be in any way due to combination between the enolic and ketonic isomerides for mixtures of the above *oxygen* ethers with the *carbon* derivatives ; *e.g.*—

$$CH_3C{=}CHCOOC_2H_5 \text{ and } CH_3CO \cdot CHCOOC_2H_5$$
$$\underset{OC_2H_5}{|} \qquad\qquad\qquad\qquad \underset{C_2H_5}{|}$$
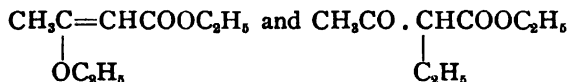
also show general absorption. There remains only the one alternative : that the absorption bands are connected with the change of one tautomeric form into the other.

The correctness of this view is confirmed by the change produced in the absorption curves of acetoacetic ester by adding varying amounts of alkali hydroxide. It is well known that the addition of alkali increases the velocity of change of these tautomerides ; in other words, it increases the number of molecules in the state of change. Moreover, it is apparent that the greater the number of molecules undergoing the change the more intense will be the absorption,

and the greater resistance will the band have to the weakening effect of dilution. This power of withstanding the effect of dilution has been called the "persistence" of the band, and a relative measure of it is obtained from the depth of the hollow in the absorption curve. Baly and Desch showed that the addition of increasing amounts of sodium hydroxide to the alcoholic solution of acetoacetic ester does actually augment the persistence of the band. The absorption curves of the solutions examined are illustrated in the annexed figure.

Oscillation frequencies.
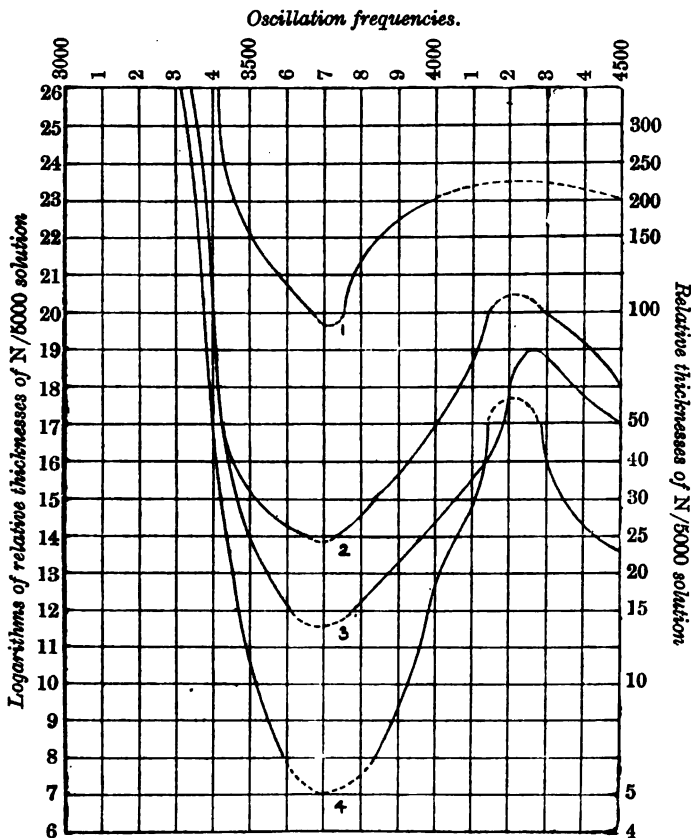
FIG. 14.

Curve 1 shows the absorption of the ester with half an equivalent of alkali, curve 2 with one equivalent, and curve 4 with an excess of alkali hydroxide. Curve 3 shows the absorption of the aluminium compound. From these results there is no doubt that the absorption band is due to the oscillation between the two isomeric forms, and it follows that the metallic derivatives consist of equilibrium-mixtures of the isomerides. On the other hand, the compounds which have no band are pure specimens of either form. It is interesting to notice that Stewart and Baly,[1] on re-examining the latter substances, found that in more concentrated solution a shallow absorption band is developed, whence it follows that the tautomeric change is present though only in slight amount. The curves for ethyl acetoacetate, ethyl laevulate and acetonylacetone are given in a subsequent figure (p. 370).

For these reasons it seems that the absorption band is due to some intramolecular oscillation which takes places when one form changes into another—

$$-CH_2-CO- \rightleftarrows -CH=C(OH)-$$
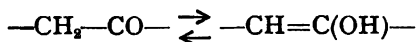
It is obvious to suggest that the vibrations are due to the rapid displacement of the labile atom from carbon to oxygen, and *vice versâ;* but this cannot be the immediate cause, since the oscillation frequency of the band does not vary to any great extent when the hydrogen of the parent compound is replaced by the heavier metals. This is particularly well illustrated by the absorption curves of acetyl acetone and its metallic derivatives (Fig. 13). It is almost inconceivable that the vibration frequency of the thorium atom should be the same as that of an atom whose mass is two hundred and thirty times as small.

Hence the band must be caused by the oscillations of the valencies, and a satisfactory explanation is afforded by the electronic theory. According to this theory, the linkage between atoms is formed by the migration of an electron or groups of electrons from the one atom to the other, and a

[1] *Trans. Chem. Soc.*, **89**, 493 (1906).

change of linkage must be accompanied by the movement of these valency electrons. Consequently the ultra-violet absorption bands of these compounds would be due to the electronic disturbance which results from the tautomeric change. The theory is further supported by the work of Drude, which has been discussed in the introduction to this chapter.

We shall now turn to another atomic grouping in which a similar connection between disturbance of valencies and absorption has been observed, and the case is the more interesting since the relations between chemical activity and absorption formed the basis of the inquiry.

§ 11. *THE DICARBONYL SYSTEM:* CO—CO

The investigation [1] of this group took origin from the work of Stewart [2] on the reactivity of the carbonyl group in the aliphatic ketones. It was found that insertion of alkyl at the α-methylene group lessens the rate of oxime and bisulphite formation. Thus far the results fell in with the current theories of steric hindrance; but when it was observed that the carbonyl group in acetoacetic ester was more reactive than that in acetone

	Per cent. of bisulphite compound formed in	
	10 mins.	40 mins.
Acetone, CH_3COCH_3	28·5	53·6
Acetoacetic ester, $CH_3COCH_2COOC_2H_5$.	37·4	60·0

it became evident that some other theory must be adopted to account for the facts. Since acetoacetic ester is known to be liable to tautomeric change, it occurred to Stewart and Baly that there might be some relation between this phenomenon and the activity of the carbonyl group. Accordingly the absorption curves (see Fig. 15) of these compounds were examined, and it was found that they show the ultra-violet band of the keto-enolic tautomeric change. Moreover, the persistence of the band decreases proportionately to the diminution of the reactivity of the —CO— group in the ketone. The following data serve to illustrate this relation :—

[1] Stewart and Baly, *Trans. Chem. Soc.*, **89**, 489 ; 502 (1906).
[2] *Trans. Chem. Soc.*, **87**, 185 (1905) ; *Proc. Chem. Soc.*, **21**, 28 (1905).

TABLE VII.

	Per cent. of oxime formed in 20 mins.
Acetone	49·7
Methyl ethyl ketone	39·2
Methyl propyl ketone	37·3
Methyl isopropyl ketone	31·5
Pinacoline	17·0

Oscillation frequencies.

I. Acetone in alcohol.
III. Acetone in water.
V. Methyl ethyl ketone.
VII. Methyl propyl ketone.

II. Methyl isopropyl ketone.
IV. Pinacoline.
VI. Methyl hexyl ketone.
VIII. Methyl nonyl ketone.
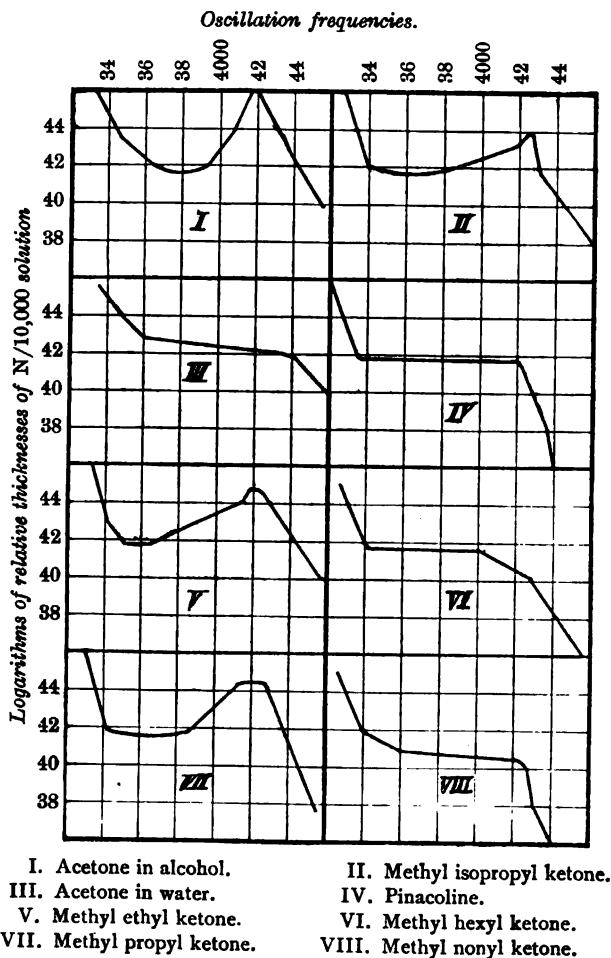
FIG. 15.

It should be observed that V. Hâncu[1] has since adduced chemical evidence showing that these simple ketones may undergo the tautomeric change in question. The close relation between the activity of the carbonyl group and the tautomeric change is thus established, and from the persistence of the band it appears that the activity of the group is roughly proportional to the amount of change going on. Stewart and Baly further point out that ·at a certain stage in the interchange of the structures

$$-CH_2-C \underset{\leftarrow}{\rightarrow} \quad -CH=C-$$
$$\underset{O}{\|} \qquad\qquad \underset{HO}{|}$$
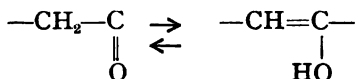
the carbonyl group will be in the nascent state, and therefore will be more reactive than the inert carbonyl of a purely ketonic substance.

Now the rate of bisulphite formation with ethyl pyruvate was found to be even greater than that of acetoacetic ester—

	Per cent. of bisulphite compound formed in		
	5 mins.	10 mins.	15 mins.
Acetone, CH_3COCH_3	5	7	9
Acetoacetic ester, $CH_3COCH_2COOC_2H_5$.	12	18	24
Ethyl pyruvate, $CH_3COCOOC_2H_5$ . . .	52	64	76

and it would seem that if this enhanced activity is due to the same cause as that of acetoacetic ester, there must be greater tendency for the CH_3—CO— group to undergo tautomeric change than in that substance. But this is contrary to chemical facts and to the evidence given by other physical properties; moreover, it may be seen in the following illustration that the absorption band of ethyl pyruvate has its head at 3100, whilst those of the ketones and acetoacetic ester lie uniformly at about 3700 units. In fact, the band of ethyl pyruvate lies nearer to the red than that of acetoacetic ester, and this shift of position cannot be due to change in mass of the molecule, since the molecule of pyruvic ester is lighter than that of acetoacetic ester. Hence the absorption band must be due to a change of linkage taking place in the —CO—COOEt grouping, and on account

[1] *Ber.*, **42**, 1052 (1909).

of the increased reactivity of the carbonyl it follows that at some time during this change of linkage the carbonyl group must exist in the nascent state. The only hypothesis which
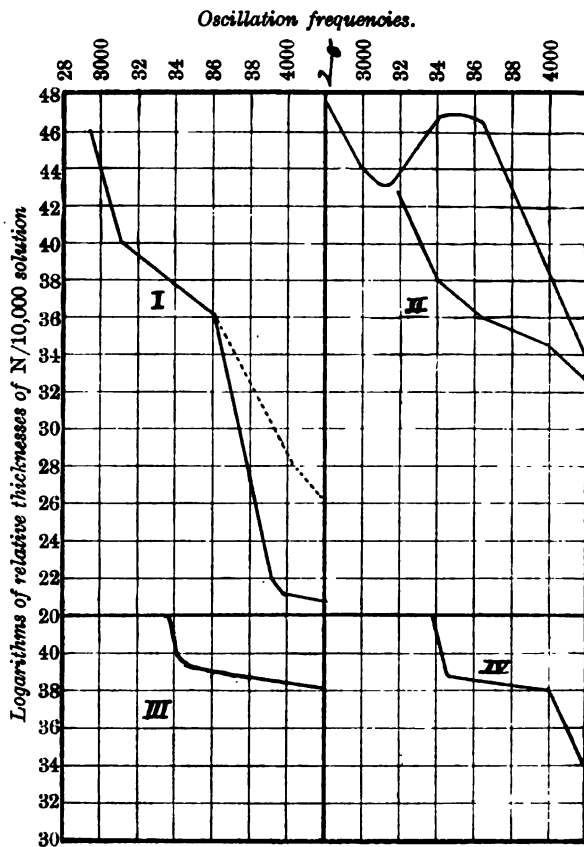
I. Ethyl acetoacetate in alcohol (full curve).
   Ethyl acetoacetate in water (dotted curve).
II. Ethyl pyruvate.
    Ethyl diethylacetoacetate.
III. Ethyl laevulate.
IV. Acetonyl acetone.

FIG. 16.

can satisfy these conditions is that the molecule of ethyl pyruvate is oscillating between the two phases—

$$CH_3—C—C—OEt \quad \underset{\longleftarrow}{\longrightarrow} \quad CH_3—C=C—OEt$$
$$\overset{\|}{O}\ \overset{\|}{O} \qquad\qquad\qquad \underset{O—O}{|\ |}$$
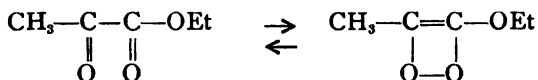
the CO group passing through the nascent condition at an intermediate stage of the process. This process differs from that of the ordinary tautomeric change by the absence of a labile atom, and for this reason Stewart and Baly propose that the word "isorropesis" (ἰσορροπία: equipoise) should be applied to it. However, it seems difficult on general grounds to distinguish between the two phenomena.

The inference that the absorption band of pyruvic ester is due to the dicarbonyl system is strikingly confirmed by the spectra of other substances containing this group, *e.g.* acenaphthene quinone, phenanthrene quinone, camphor quinone, benzil, and diacetyl. The last-named compound affords the best illustration (Fig. 17), since the structure is not complicated by benzene nuclei, and it is important to observe that when the dicarbonyl system is destroyed by conversion to the dioxime the absorption band disappears. In these substances the absorption bands lie nearer the red portion of the spectrum than in ethyl pyruvate; in fact, they occur in the visible spectrum at about 2100–2400 units, so that the compounds appear coloured. We see, then, that the dicarbonyl system functions as a chromophore, and that this "isorropesis" may give rise to colour in organic compounds.[1]

§ 12. *THE QUINONOID SYSTEM*

Stewart and Baly[2] at once extended these ideas to *p*-benzoquinone and its simple derivatives. In *p*-benzoquinone there

[1] The hypothesis of isorropesis has been extended to the isonitroso compounds —C—C— of the fatty ketones. See Baly, Marsden and Stewart,
$$\overset{\|}{O}\ \ \overset{\|}{NOH}$$
Trans. Chem. Soc., **89**, 966 (1906).

[2] *Trans. Chem. Soc.*, **89**, 506 (1906); Stewart and Baly, *Trans. Chem. Soc.*, **89**, 618 (1906).

are two carbonyl groups in the 1·4 positions of a six-membered ring, and it is remarkable that whilst in diacetyl, where these

Oscillation frequencies.

Full curve = diacetyl.   Dotted curve = diacetyldioxime.
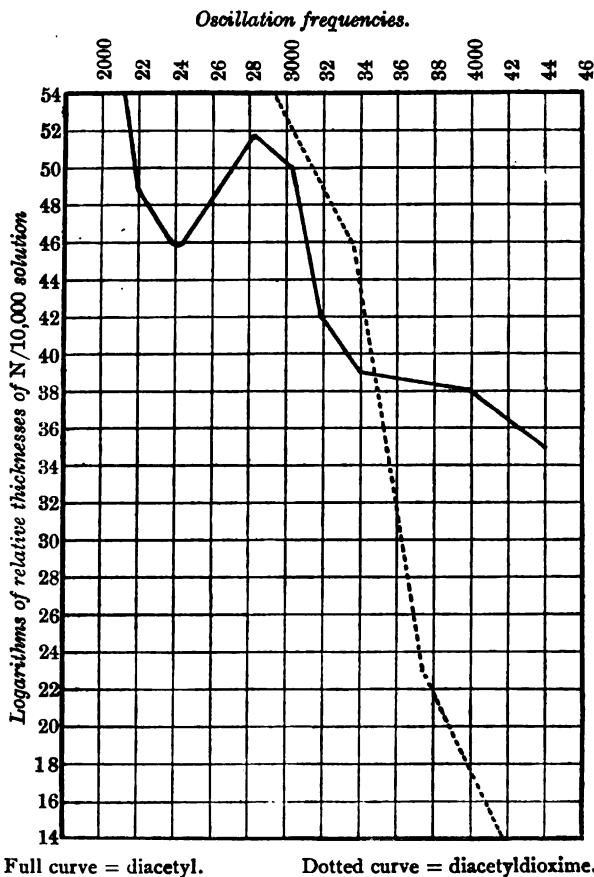
FIG. 17.

groups are adjacent, there is no chemical evidence for the peroxidic structure

$$-C==C-$$
$$\ \ |\ \ \ \ |$$
$$\ \ O-O$$
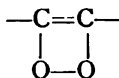
this ·has long been suspected in the cyclic compound. In fact, Graebe[1] proposed that quinone should be written as a peroxide (I.), whilst Fittig[2] supports the ketonic formula (II.).
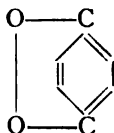
I. II.

It may be mentioned that the typical reactions favouring these alternative formulæ are the action of phosphorus penta-chloride, which furnishes *p*-dichloro-benzene (peroxidic struc-ture), and the action of hydroxylamine, which yields quinone dioxime (ketonic structure). It will be seen from these formulæ that the peroxide is a true benzene compound, whilst the dike-tone is a derivative of tetrahydrobenzene.

Now the absorption curve of quinone bears out the chemical evidence, since it shows two bands, the one in the ultra-violet with its head at about 4000, and the other in the visible region at about 2300 units. From its position the latter is evidently the isorropic band caused by the oscillations of valency in the dicarbonyl system, whilst the former occurs in the position of the characteristic benzenoid bands,[3] and is therefore due to the oscillations peculiar to this structure. The dual nature of the absorption of the *p*-benzoquinones is best illustrated by the curve of thymoquinone, in which the two characteristics are fairly evenly balanced (p. 374, Fig. 18).

With quinone in alcoholic solution the isorropic condition seems to predominate, and the benzene band is not well marked ; but it should be noticed that Hartley and Leonard[4] have shown

[1] *Zeit. für Chem.*, **3**, 39 (1867).

[2] *Ann.*, **180**, 23 (1876).

[3] See p. 385.

[4] *Trans. Chem. Soc.*, **95**, 45 (1909).

that the two bands are distinctly formed with ethereal solutions of the substance.

Kehrmann[1] has demonstrated that the reactivity of the

Oscillation frequencies.
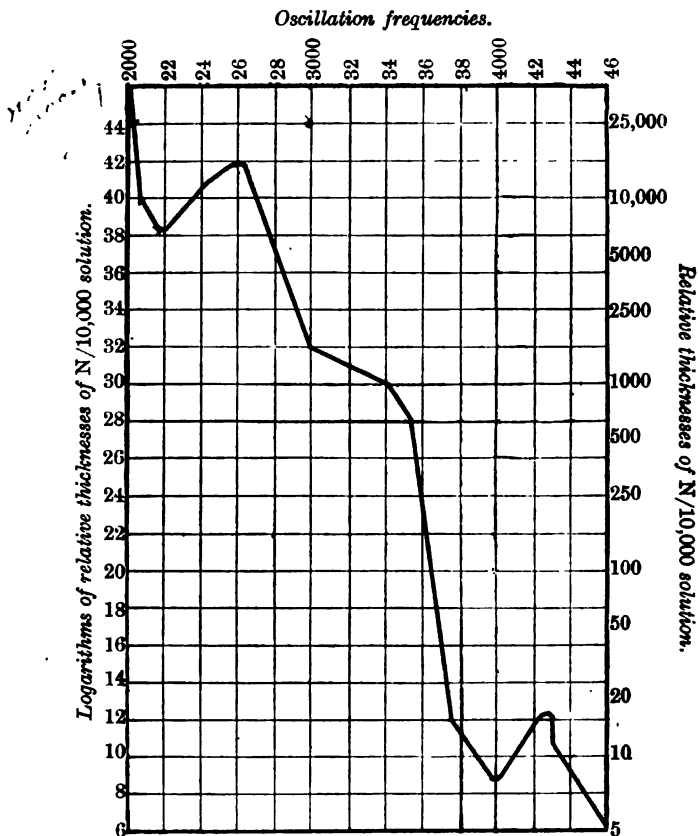
FIG. 18.

carbonyl groups in *p*-benzoquinone is lessened by substituting the hydrogen atoms with methyl or halogen. In fact, the substituted quinones, when arranged according to descending activity of oxime formation, fall into the following order :—

[1] *Ber.*, **21**, 3315 (1888) ; *Journ. Pr. Chem.*, **39**, 399 ; **40**, 257 (1889).

p. Benzoquinone . . . forms dioxime easily.

Mono substituted . . . forms dioxime less easily.

2·5 Disubstituted . . . form mono and dioxime with
difficulty.

2·6 Disubstituted . . . form monoximes only.

Trisubstituted . . . . form monoximes only.

Tetrasubstituted. . . . form no oximes.

The absorption curves of the following series of quinones in alcoholic solution

| Chlorobenzo-quinone. | 2·6 Dichloro-benzoquinone. | Trichloro-benzoquinone. | Trichloro-toluquinone. |
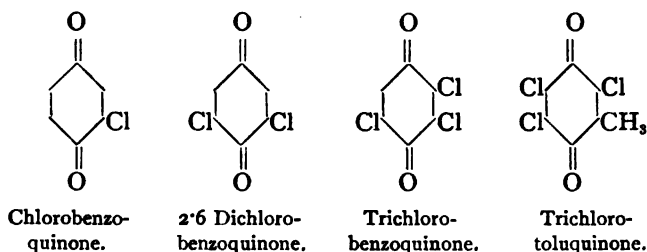
are shown in the figures[1] on p. 376, and it will be seen that the band due to the dicarbonyl groups diminishes as substitution proceeds. In chlorobenzoquinone the band has become merely a slanting line, in the dichloro-compound the line representing it almost follows the line of the curve, and in trichlorobenzoquinone and trichlorotoluquinone it cannot be detected. At the same time the persistence of the benzenoid band increases steadily, as can be seen from the following data :—

CHANGE OF DILUTION OVER WHICH THE BAND PERSISTS WITH

Monochlorobenoquinone . . . . . . 42·0 per cent.

2·6 Dichlorobenzoquinone . . . . . . 55·0 ,,

Trichlorobenzoquinone . . . . . . 77·0 ,,

Trichlorotoluquinone . . . . 88·0 ,,

It may be observed in passing, that increasing the number

[1] The curves are reproduced with permission from Stewart's *Recent Advances in Inorganic and Physical Chemistry*, Longmans & Co.
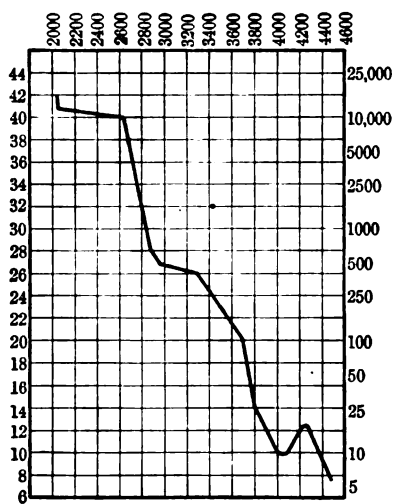
Chlorobenzoquinone.
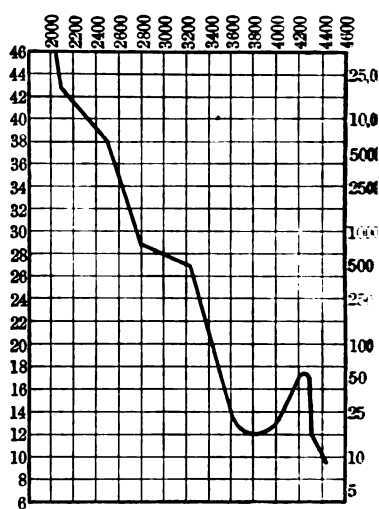
Dichlorobenzoquinone.
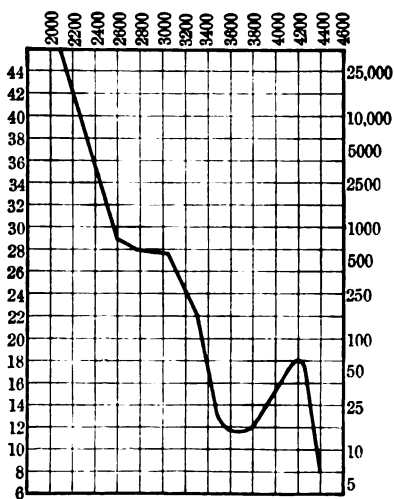
Trichlorobenzoquinone.
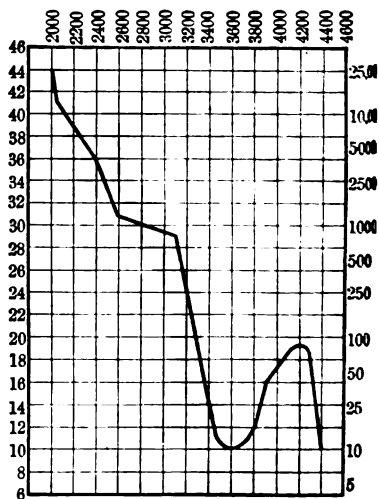
Trichlorotoluquinone.

FIG. 19.

of the halogen atoms slightly shifts this band towards the red ; but this is the usual effect of weighting the molecule.

We see, then, that not only the reactive power of the characteristic groups, but also the actual intramolecular state of these compounds can be detected in their absorption spectra.

It is evident that increasing substitution tends to establish the permanent benzenoid structure of the peroxidic form, thus preventing the " isorropic " process :
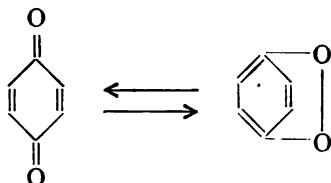
and the consequent nascence of the carbonyl groups.   Stewart and Baly consider that this effect of substitution is the result of several factors, of which the chief is the disturbance of the normal vibrations of the system.   When unloaded there is no doubt that the vibrations of the ring would be parallel to the plane of symmetry of the molecule ; but when a substituent is inserted a new plane of symmetry would be formed and the vibration correspondingly altered. Another factor, undoubtedly, is the disturbance produced in the balance of affinities in the unsaturated system by the residual affinity of the substituent. The effect of substitution in the benzene system is discussed in a subsequent portion of this chapter.

It is clear that the colour of the quinones is due to the vibrations set up by the oscillating valencies in the equilibrium between the true carbonyl and the benzenoid structures.   The discovery made by Willstätter,[1] that *o*-benzoquinone exists in both colourless and coloured modifications is of great interest. Evidently the colourless compound consists of one form or other in the pure state, whilst the coloured isomeride would be an equilibrium mixture of the two.

[1] Willstätter and Müller, *Ber.*, **41**, 2580 (1908).
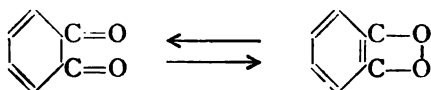
Chemists have not been slow in applying these theories to other coloured compounds in which the quinonoid structure has been suspected.

All hydroxy and amino derivatives of triphenyl-carbinol are colourless, but they may be transformed into coloured compounds by loss of the elements of water, *e.g.* :—

p Oxyphenyl diphenyl   Fuchsone.
     carbinol.   Yellow.
     Colourless.
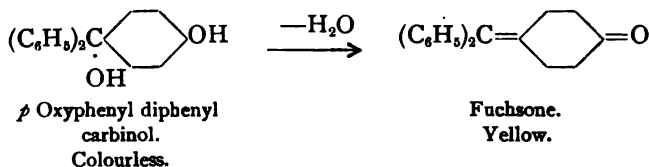
Baeyer[1] has observed that the amino compounds which contain only one amino group in the para position to the methane carbon atom give weakly coloured dye-salts ; the characteristic colour of the rosaniline dye-stuffs is not obtained until at least two such amino groups are present. This relation may be illustrated by the following dye-salts—

Fuchsonimonium   Döbner's violet.
   chloride.
   Orange.   Orange.
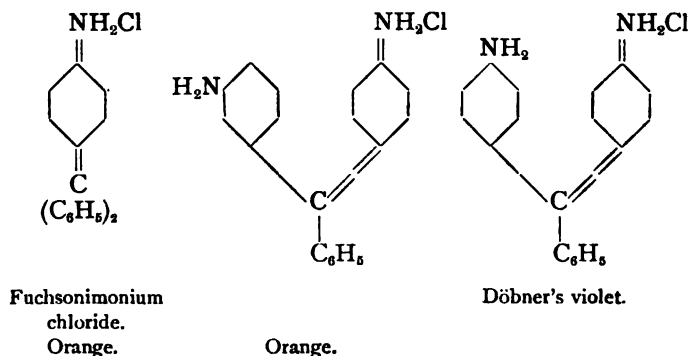
[1] *Ann.*, **854**, 152 (1907).

and it will be seen that the dye-salt obtained from the meta-para diamino compound is weakly coloured in comparison with Döbner's violet, the di-para derivative. Similar relations hold with the hydroxyl derivatives. Baeyer then examined the absorption spectra of these substances and, as might be expected, he found the same relations as with colour. The characteristic selective absorption of the triphenyl methane dyes[1] is not formed until at least two of the benzene nuclei contain a para substituent (OH or NH_2). Moreover, when all three benzene complexes are substituted in this position, the absorption bands become more intense and more sharply ·defined.

Now the absorption spectra of the amino dye-salts are the same as those shown by the alkali salts of the corresponding oxy compounds. The spectra of the sodium salt of benzaurine and of Döbner's violet are identical.
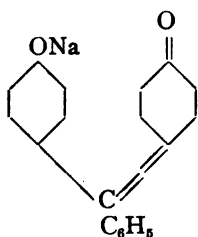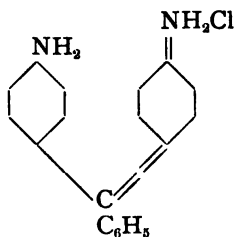
Benzaurine.   Döbner's violet.

It follows that the amino and hydroxyl groups are not immediately responsible for the absorption, but this must instead be due to the condition of the benzene nuclei. Further, it is evident that the dynamic process which causes the absorption must concern at least two of the aromatic nuclei. Baeyer points out that this state of affairs is best represented by supposing the quinonoid structure to be oscillating between the substituted nuclei, and he expresses this by formulæ such as—

[1] See also Hartley, *Trans. Chem. Soc.*, **51**, 152 (1887).

$$NH_2 \quad Cl \quad NH_2$$

$$\overset{|}{C_6H_5}$$
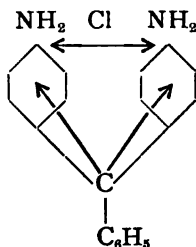
Döbner's violet.

in which the arrows represent the oscillating valencies.

Similar results were obtained by Willstätter, who, as we have already seen, investigated the composition of the red dye-stuff formed by oxidizing *p*-amino-dimethylaniline. Willstätter's experiments led him to conclude that the colour of this dye-stuff and those of the triphenyl methane series is due to the *meri*quinonoid state of the molecule; and this condition is attained in a balance between the true quinonoid and the benzene structures.

It will now be clear that the researches of Stewart and Baly, of von Baeyer, and of Willstätter, lead to similar conclusions. The first-named investigators showed that the absorption of the simple quinones (Willstätter's holoquinones) is due to an equilibrium between the true carbonyl form and some benzenoid structure; here the equilibrium is intramolecular and intranuclear. In Würster's red (the meriquinones) the equilibrium is internuclear and intermolecular; whilst in the triphenyl methane dyes it is intramolecular and internuclear.

Before concluding the study of this subject, it must be observed that the precise nature of the relations between intramolecular change and absorption is by no means exactly known. Lowry and Desch[1] have recently attacked the question from a general standpoint. From their investigation of nitrocamphor and its derivatives it is clear that there are at least some types of isomeric change which do not produce

[1] *Trans. Chem. Soc.*, **95**, 807 (1909).

selective absorption. Lowry [1] has shown that the speed of change between the normal and ψ nitrocamphor

$$C_8H_{14}\left\langle\begin{matrix}CH-NO_2\\ |\\ CO\end{matrix}\right. \quad\begin{matrix}\leftarrow\\ \rightarrow\end{matrix}\quad C_8H_{14}\left\langle\begin{matrix}C=NO_2H\\ |\\ CO\end{matrix}\right.$$

Normal nitrocamphor.   Pseudo nitrocamphor.
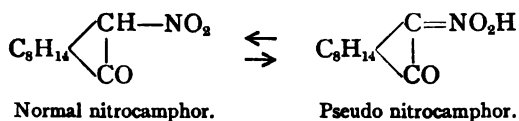
can be regulated at will by the choice of solvent or the addition of suitable reagents, and it is thus possible to examine solutions in which isomeric change is either arrested or is proceeding with varying speed. However, Lowry and Desch find that the absorption curves of all these solutions of nitro-camphor are very similar, and that none show selective absorption. When alkali is added to the solution a deep band is developed, with its head at about 3100 units. But this cannot be due to isomeric change, for in presence of alkali the conversion of nitrocamphor to the sodium salt of the pseudo form is complete, and excess of the reagent produces no change in the band. This, it will be remembered, is contrary to the effect of increasing amounts of alkali on the absorption band of acetoacetic ester. Lowry and Desch consider that here the band is due to the structure of the sodium salt, which is different from that of the pseudo or normal forms, and they suggest that these compounds should be represented as follows :—

$$C_8H_{14}\left\langle\begin{matrix}CH.NO_2\\ |\\ CO\end{matrix}\right. \begin{matrix}\rightarrow\\ \rightleftharpoons\\ \leftarrow\end{matrix} C_8H_{14}\left\langle\begin{matrix}C\langle{}^O_{N.OH}\\ |\\ CO\end{matrix}\right. \rightarrow C_8H_{14}\left\langle\begin{matrix}C=\overset{O}{\overset{\|}{N}}.ONa\\ |\\ C=O\end{matrix}\right.$$

Normal form.   Pseudo form.   Sodium salt (*red*).
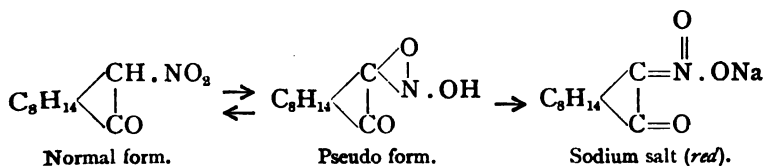
It will be seen that the red salt contains a conjugated system of unsaturated linkages, and Lowry and Desch think it is probable that this arrangement is responsible for the absorption band, for the salts of the similarly constituted

[1] *Trans. Chem. Soc.*, **75**, 219 (1899) ; **85**, 1541 (1904) ; **93**, 107 (1908).

nitro camphane, which do not contain this system, do not show ·

$$C_8H_{14} \diagup \overset{CH_2}{\underset{CH \cdot NO_2}{|}}$$

Nitro-camphane.

$$C_8H_{14} \diagup \overset{CH_2}{\underset{C=NOONa}{|}}$$
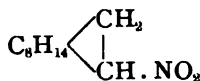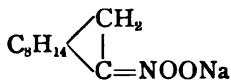
Sodium salt.

selective absorption. As bearing on the question whether a conjugated system may give rise to a selective absorption, it should be noticed that Wallach [1] has found that all compounds containing the grouping

$$> C = CH - CO -$$

show selective absorption in the violet region.

Moreover, many derivatives of camphor which contain the two α hydrogen atoms replaced by halogen or methyl, as in

$$C_8H_{14} \diagup \overset{CBr \cdot CH_3}{\underset{CO}{|}}$$
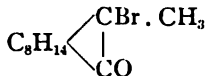
a Bromo-methyl-camphor.

show a distinct absorption band. If, as Lowry and Desch aver, all isomeric change is excluded by this substitution, it follows that selective absorption may be caused by other conditions than those set up by tautomeric change.

Enough has been said to show that much research is yet to be done before the exact relations between absorption and tautomeric change can be defined.[2] If the interpretation given by Baly and Desch be correct, and there seems no reason to doubt it, it seems that we must await the application of the electronic theory to organic chemistry before a general advance can be made.

---

[1] *Chem. Centralblatt.*, **1**, 372 (1897).

[2] For further evidence on the question the reader should consult Hartley, *Trans. Chem. Soc.*, **87**, 1818, 1826 (1905); and Schmiedlin, *Compt. Rend.*, **139**, 872 (1904). The latter gives a physical theory of the origin of colour.

§ 13. *THE BENZENE SYSTEM*

At a quite early stage in the discussion of the structure of benzene it was recognized that some oscillation of valency must be continually going on in the atomic system of this substance. Although many structural formulæ were from time to time put forward, it was not till 1897 that the dynamic condition of the benzene system was thoroughly examined. Collie [1] then showed that by considering the various possible movements and the spatial relations of the carbon atoms, the properties of benzene and its derivatives may be fully accounted for, and further that the Kekulé, centric, and diagonal formulæ appear to be phases in the motion of the system. Since Baly and Desch had found that the oscillations of valency in the equilibrium of keto-enolic tautomerides gives rise to an absorption band, it seemed possible that further information on the vibrations of the benzene molecule might be obtained from the study of its absorption spectrum. Baly and Collie [2] therefore joined forces in the research. During the tautomeric change which takes place between the keto-enol isomerides there is a make and break of linkage between two carbon atoms

$$-\overset{*}{C}H_2-\overset{*}{C}-\\ \underset{O}{\overset{\|}{}}$$
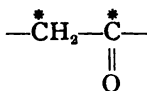
But in the benzene system there will be many different kinds of this make and break of valency, according as the different carbon atoms approach and recede from one another in the various phases of motion.

According to Baly and Collie there are altogether seven different kinds of these phases possible. These are illustrated in the following diagrams, the carbon atoms marked with a star being those between which the make and break of linkage is occurring.

[1] *Trans. Chem. Soc.*, **71**, 1013 (1897).
[2] *Trans. Chem. Soc.*, **87**, 1332 (1905).
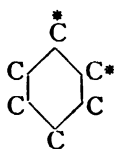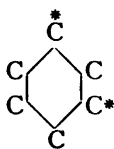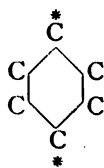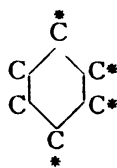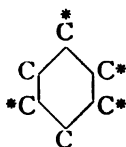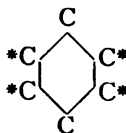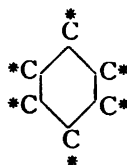
The absorption curve of benzene is very complex; in fact, as Hartley and Huntington [1] showed, it contains seven bands, and it will be noticed (see Fig. 22) that this number exactly corresponds to the possible forms of change of linkage.[2] Assuming that this coincidence is not due to chance, it is clear that the absorption bands of benzene may be fully explained by the changes of linkage which are going on in the molecule, although it is impossible to attribute any individual band to any particular one of the seven phases. Collie's theory of the vibrations in the benzene system was later developed [3] by Baly, Edwards, and Stewart,[4] who pointed out that the various phases must be brought about by the displacement of the carbon atoms of the ring. The simplest way of explaining this is to assume that the cyclic chain of atoms is vibrating in the ordinary manner of an elastic ring. It is

[1] *Phil. Trans.*, 170, 1, 257 (1879); also Hartley and Dobbie, *Trans., Chem. Soc.*, 73, 695 (1898); and Hartley, *Proc. Roy. Soc.*, 80, 162 (1908).

[2] It should be observed that Hartley has recently shown (*Proc. Roy. Soc.*, 80, 162 (1907)) that the absorption spectrum of benzene vapour exhibits a larger number of bands.

[3] *Trans. Chem. Soc.*, 89, 514 (1906).

[4] Hartley, *Trans. Chem. Soc.*, 87, 1826 (1905), has put forward a imilar theory to account for six bands in the benzene spectra.

then evident that there will be two extreme phases of maximum displacement as represented in the figures *a* and *b*.
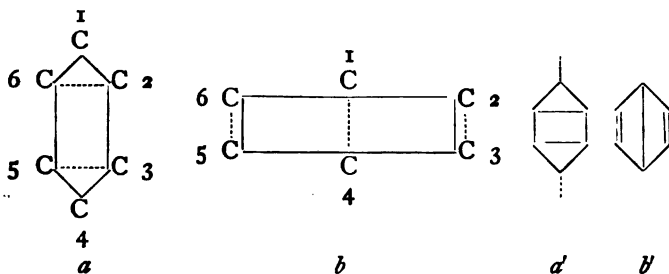
In the condition represented by *a*, when the atoms 2 and 6 and the atoms 3 and 5 are brought close together, the residual affinities of these will unite to form temporary linkages, as shown by the dotted lines. The atoms 1 and 4 will approach the unsaturated condition, since they are far removed from one another. In the other phase, shown in figure *b*, the atoms 1 and 4, 2 and 3, and 6 and 5 will closely approach one another, and temporary linkage between these pairs of atoms may be assumed. These extreme phases are drawn on the usual scheme in figures *a'* and *b'*, and it will be noticed that the extreme phase *b'* is identical with the Dewar formula for benzene. Making certain assumptions as to changes in the axis of displacement, the occurrence of each of the seven phases may be satisfactorily explained, and it is interesting to observe that at the half-way stage, *i.e.* when the configuration is regular, the condition of the molecule will be identical with that shown in the centric formula.
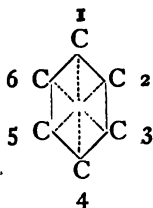
Further support is lent to this theory of the vibrations of the

benzene system by the explanation it affords of the chemical behaviour of certain substitution products. A single case must suffice to illustrate this point. It is clear that in a compound such as terephthalic acid that the pulsation of the ring

COOH

COOH

H.C.COOH
CH⟨ ⟩CH
CH⟨ ⟩CH
H.C.COOH
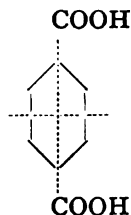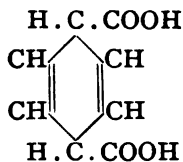
Terephthalic acid. $\Delta^{2.5}$ Dihydroterephthalic acid.

will take place readily along the axes marked in the figure, and this vibration of the benzene system will be less disturbed by para substitution than by ortho or meta. Consequently terephthalic acid will exist to a certain extent in the phase shown in *a*, where the 1·4 carbon atoms are unsaturated. Additive reagents should therefore be readily taken up at these atoms. In practice terephthalic acid is found to be more easily reducible than phthalic and isophthalic acids, and the first product formed is the $\Delta^{2.5}$ dihydro-derivative. Another interesting deduction to be made from this theory is the possibility of the transitory existence of *meta*-quinones. If in a substance like *m*-nitrophenol, the displacement of the ring takes place on the axes marked by the dotted lines (Fig. 1)

HO⟨ ⟩NO₂   HO⟨ ⟩NO₂   O=⟨ ⟩=NO₂H
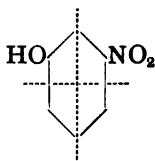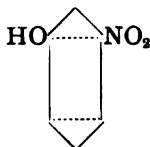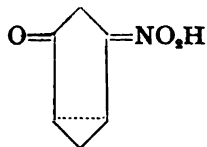
1.   2.   3.

the phase represented in Fig 2 will be reached, and whilst in this phase the *meta*-quinone (Fig. 3) may exist. Moreover, the existence of the unstable meta-quinones seems almost certain from the measurements of the absorption spectra of *meta*-

nitraniline and nitrophenol,[1] and from the later work of Hantzsch[2] on the salts of various *meta*-nitro phenols.
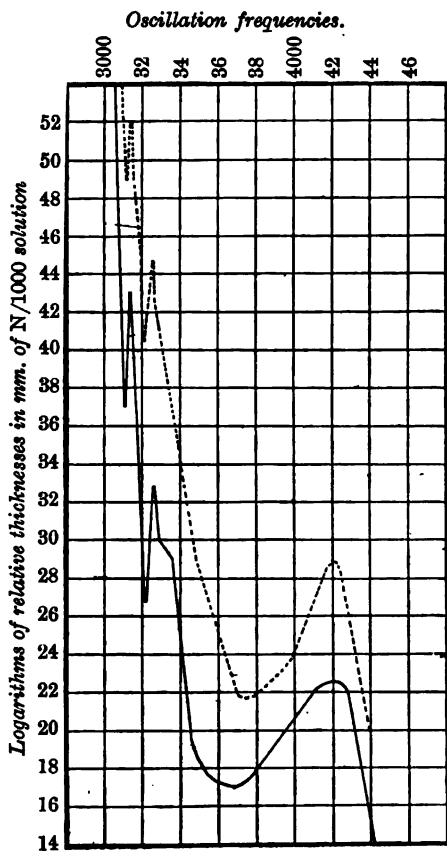
FIG. 20.

Full curve, Naphthalene.   Dotted curve, Dihydronaphthalene.

Baly and Tuck[3] consider it probable that the naphthalene molecule undergoes similar pulsations. Naphthalene shows

[1] Baly, Edwards and Stewart, *Trans. Chem. Soc.*, **89**, 520 (1906).

[2] Hantzsch, *Ber.*, **40**, 330 (1907).

[3] *Trans. Chem. Soc.*, **93**, 1906 (1908).

three bands : two narrow ones with heads at 3125 and 3220 units respectively, and a broader band with its head at 3700 units. It is almost certain that the last-named band is due to the ben-

Oscillation frequencies.
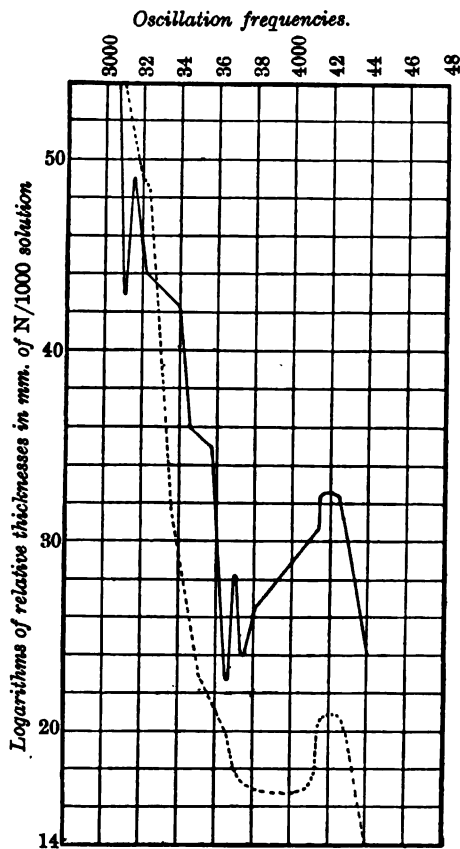
FIG. 21.

Full curve, α-Tetrahydronaphthalene
Dotted curve, Tetrahydronaphthalene.

zenoid vibrations of one nucleus, since it is contained in the spectrum of tetrahydronaphthalene (Fig. 21), and it occupies the same position as the absorption bands of benzene. The two

smaller bands seem due to some disturbance exerted by the unsaturated atoms of the aliphatic ring on the unsaturated affinities of the benzenoid half of the molecule ; and it is clear that this disturbance is due to the carbon atoms marked 2 and 3 (*a*), for dihydronaphthalene (*c*) shows the two bands in question.

a   *b*   *c*
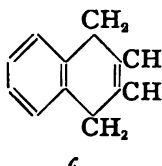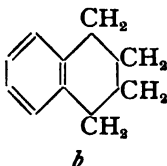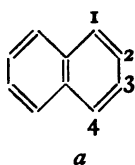
These relations may be explained by considering the pulsations of the naphthalene system. The following diagrams represent the molecule in the two extreme phases—

d   *e*
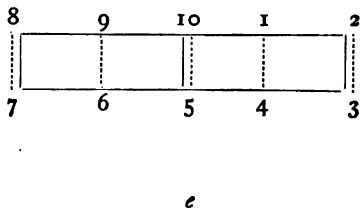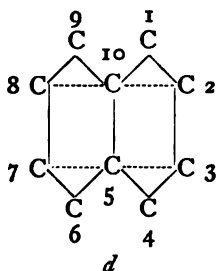
Assuming that at an intermediate stage the left half of the molecule is temporarily in the benzenoid state, it is clear that then the atoms 1 and 4 of the ethenoid half do not disturb the residual affinities of the atoms in the benzenoid half. It is further evident that the disturbance is caused by carbon atoms 2 and 3, and that it will reach a maximum while the molecule is passing through stage *d*. The absorption spectra of naphthalene and its hydro-derivatives are thus fully explained by the pulsation theory. For the further application of this hypothesis to azobenzene,[1] hydroxyazo-compounds[2] and

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[1] Baly and Tuck, *Trans. Chem. Soc.*, **89**, 983 (1906).

[2] Tuck, *Trans. Chem. Soc.*, **91**, 449 (1907).

derivatives of pyridine,[1] the reader must be referred to the original literature.

In the preceding paragraphs we have endeavoured to trace the cause of selective absorption in the dynamic condition of the linkages between the atoms; we shall now in turn examine the general influence of substitution on these absorption bands.

B.—2. Visible and Ultra-Violet Absorption—*continued*

§ 14.—(*c*) *The Influence of Substitution on Absorption*

The question as to the effect of substitution on absorption was attacked long before the cause of the phenomenon had been explained, and there naturally resulted a series of empirical rules. As might be expected when dealing with a constitutive property like absorption, the rules established were not general, and they hold only within the groups of compounds from which they have been deduced. It will therefore be of little benefit to follow these results in detail, and we shall instead confine our attention to the broader aspects of the question.

The more recent work on the subject has shown that substitution may influence the absorption of the parent compound in two ways, either by the mass or by the residual affinity of the substituent.

i. *The Influence of the Mass of the Substituent*

The increase in mass of the molecule which occurs on the insertion of a substituent tends to retard the intramolecular vibrations, and so brings the absorption towards the red portion of the spectrum. This rule was first laid down by Hartley[2] as the result of his extensive researches on ultra-violet absorption; but it holds also with visible absorption

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[1] Baly and Baker, *Trans. Chem. Soc.* **91**, 1122 (1007); Purvis, *Trans. Chem. Soc.*, **95**, 500 (1909).

[2] *Trans. Chem. Soc.*, **39**, 165 (1881); **47**, 693 (1885); **83**, 244 (1903).

and possibly with the infra-red. Moreover, the law holds with compounds which differ widely from one another in chemical nature ; for example, it has been observed with colourless aliphatic compounds such as the alcohols,[1] amines,[2] alkyl nitrates,[3] etc., with dye-stuffs of the indigo,[4] thionine,[5] alizarine,[6] and other groups, and with derivatives of benzene and of pyridine.[7] Attempts have been made to express quantitatively the shift in the spectrum caused by certain substituents ; but we may pass these over without notice, since it is clear from the constitutive nature of the property that no constant value can be assigned to the effect of any given group.

Generally speaking the influence of substitution with a particular group is greater on substances of low molecular weight than on complex bodies. In fact, Dobbie and Lauder [8] have shown that insertion of methyl and other light groups has no effect on the absorption spectra of complex alkaloids.

Besides merely slowing down the general vibrations of the molecule, the mass of the substituent may act in another manner : by disturbing the symmetry relations of the molecule, when it may entirely alter the character of the spectrum. The effect in question has been studied only in cyclic systems such as those of benzene [9] or of pyridine.[10] We have seen that according to the theory put forward by Baly, Edwards, and

[1] Schönn, *Wied. Ann.*, **6**, 747 (1879).

[2] Russell and Lapraik, *Trans. Chem. Soc.*, **39**, 168 (1881).

[3] Soret and Rilliet, *Compt. Rend.*, **89**, 747 (1879).

[4] Krüss, *Zeit. Phys. Chem.*, **2**, 312 (1888) ; Krüss and Allhause, *Ber.*, **22**, 2065 (1889).

[5] Bernthsen and Goske, *Ber.*, **20**, 931 (1887).

[6] Krüss, *loc. cit.*, and Liebermann and Kostanecki, *Ber.*, **21**, 2527 (1888).

[7] Hartley, *Trans. Chem. Soc.*, **47**, 685 (1885) ; Purvis, *Trans. Chem. Soc.*, **95**, 294 (1909) ; Baly and Baker, *ibid.*, **91**, 1122 (1907).

[8] *Trans. Chem. Soc.*, **83**, 612 (1904) ; see also p. 332.

[9] Baly and Ewbank, *Trans. Chem. Soc.*, **87**, 1355 (1905); Baly and Collie, *Trans. Chem. Soc.*, **87**, 1345 (1905) ; Stewart and Baly, *ibid.*, 8 ; Baly, Edwards and Stewart, *ibid.*, **89**, 527 (1906).

[10] Purvis, *Proc. Camb. Phil. Soc.*, **14**, 568 (1908); *Trans. Chem. Soc.*, **95**, 294 (1909) ; Baly and Baker, *Trans. Chem. Soc.*, **91**, 1122 (1907).

Stewart the benzene ring is pulsating as an elastic ring between the two phases a and b.

a b
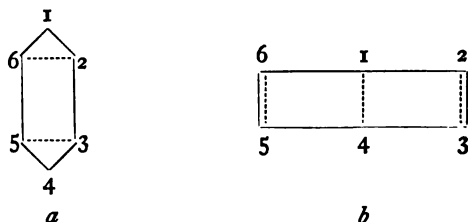
It is evident that if a single neutral substituent is attached to the ring these vibrations will not be disturbed to any great extent, and the ring will continue to pulsate in much the same
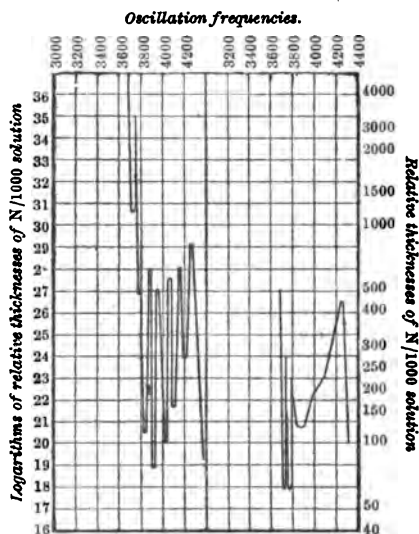
FIG. 22.

Left-hand curve, Benzene.
Right-hand curve, Toluene, etc.

way as before. To illustrate this we may take the absorption curve of toluene, which is shown side by side with that of benzene in Fig. 22.

We see that in toluene the absorption is very slightly shifted towards the red, but the general character of the more persistent benzenoid absorption is unchanged except for the merging of three narrow bands into a broader one.

Again, on comparing the three types of disubstituted derivatives, it will be recognized that the pulsation of the ring
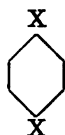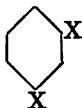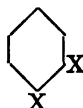
Para.　　　　　Meta.　　　　　Ortho.

will be less disturbed by para substitution than by either the meta or ortho. The absorption spectra of the isomerides are in

Ortho-　　Meta-　　Para-
　　　　Xylenes.
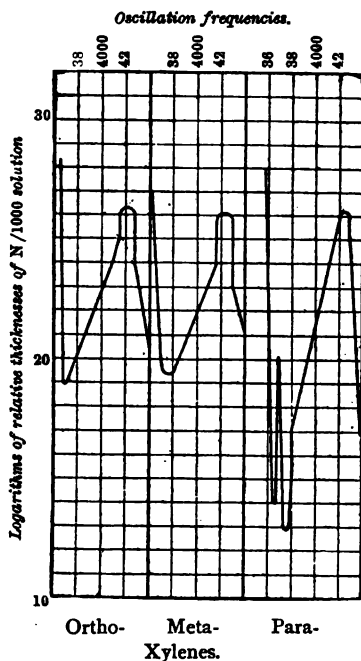
FIG. 23.

accord with these deductions from theory. Baly and Ewbank have shown that in every case the absorption curve of the para compound shows either more of the benzenoid bands than the ortho or meta compounds, or the same number with a much greater persistence. The curves in Figs. 23 and 24 illustrate the absorption of the three xylenes and the chloroanilines, the latter being taken in presence of excess of acid in order to diminish the effect of the unsaturated amino group.

Ortho-   Meta-   Para-
Chloroanilines in acid solution.
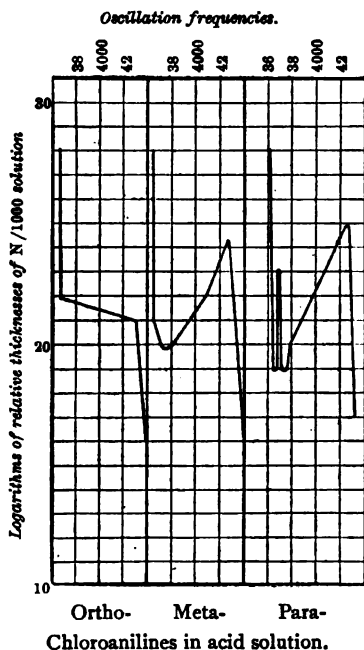
FIG. 24.

Also in the pyridine series, the spatial position of the substituents influences the form of the absorption curves. The effect may be illustrated with the chlorine derivatives. Pyridine exhibits a well-defined band with head at about 3950 units, and the normal effect of attaching chlorine to the ring is to increase the persistency of this band and to shift it

towards the red. The shift in the position of the band can be clearly seen on inspecting the following list :—

	Position of band.
Pyridine	3950[1]
3, 5 dichloropyridine	3700[2]
3, 4, 5 trichloropyridine	3650[2]
2, 3, 5 trichloropyridine	3580[2]
2, 3, 4, 5 tetrachloropyridine	3500[3]
Pentachloropyridine	3400[3]

Now, on comparing the two trichloro-derivatives
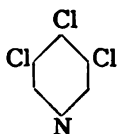
Cl
Cl⟨⟩Cl
N
3, 4, 5 Dichloropyridine.
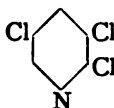
Cl⟨⟩Cl
Cl
N
2, 3, 5 Trichloropyridine.

it is seen that the disturbance, *i.e.* the displacement and change in persistence, of the pyridine band is less in the symmetrical compound than in the unsymmetrical. This may be explained by supposing the vibrations of the pyridine system to be less disturbed by symmetrical than by unsymmetrical substitution. Unfortunately only one other comparison of this nature can at present be made; but here the same relations hold. In the two tetrachloro-amino-pyridines
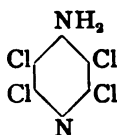
NH_2
Cl⟨⟩Cl
Cl⟨⟩Cl
N
Tetrachloro 4 amino-pyridine.
Band at 3550.[4]
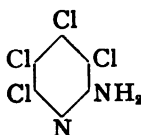
Cl
Cl⟨⟩Cl
Cl⟨⟩NH_2
N
Tetrachloro 2 amino-pyridine.
Band at 3050.[4]

[1] Hartley, *Trans. Chem. Soc.*, **47**, 685 (1885).
[2] Purvis, *Proc. Camb. Phil. Soc.*, **14**, 568 (1908).
[3] Baker and Baly, *Trans. Chem. Soc.*, **91**, 1124 (1907).
[4] Purvis, *Trans. Chem. Soc.*, **95**, 296 (1909).

the band is shifted less towards the red in the symmetrical 4 amino compound than in the unsymmetrical 2 derivative.

At present no definite scheme has been brought forward to represent the movements of the pyridine system, but on account of the presence of the highly unsaturated nitrogen atom there can be little doubt that the vibrations must be different from those of the benzene nucleus.

ii. *The Influence of the Residual Affinity of the Substituent*

To illustrate the influence of the residual affinity of the substituent on absorption we shall again employ the derivatives of benzene,[1] and by adhering solely to the mono-

Aniline with hydrochloric acid.   Anisole.

Fig. 25.

Aniline.   Acetophenone.
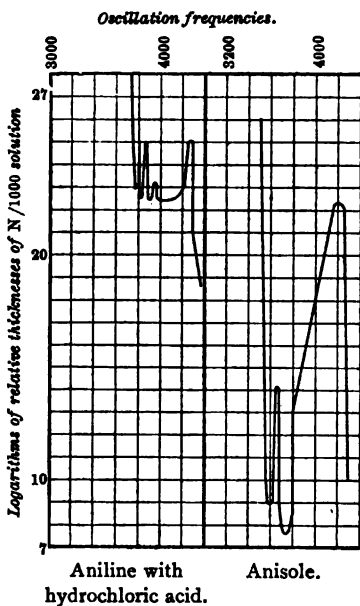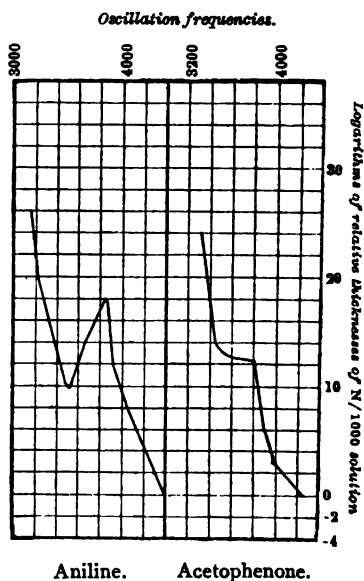
Fig. 26.

[1] Baly and Collie, *Trans. Chem. Soc.*, **87**, 1332 (1905); Hartley and Huntington, *Phil. Trans.*, **170**, 1, 257 (1879); *Proc. Roy. Soc.*, **31**, 1 (1880); Hartley and Hedley, *Trans. Chem. Soc.*, **91**, 314, 319 (1907); Baly and Ewbank, *Trans. Chem. Soc.*, **87**, 1347, 1355 (1905).

substitution products, the disturbing influence of the mass of
the group will be as far as possible eliminated. In these
substances the absorption bands of benzene are not to any
great extent disturbed if saturated atoms are attached to the
nucleus, but with unsaturated atoms the disturbance is very
marked. For illustration of the former rule, the curves of
benzene and toluene shown in Fig. 22 on a previous page
may be compared, and in evidence of the influence of unsatu-
rated groups the following diagrams may be consulted.

Benzaldehyde.   Nitrobenzene.
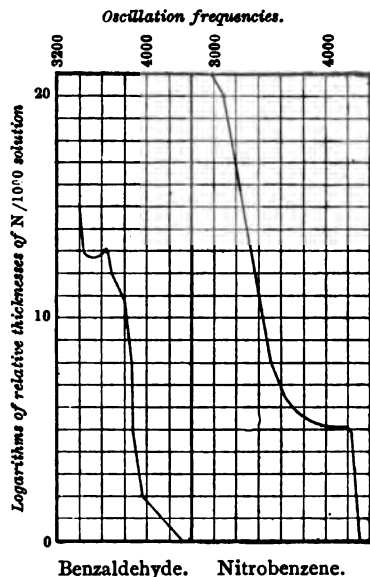
FIG. 27.

It will be seen that with anisole, which contains the
methoxyl group, the benzene spectrum still appears, though in
a modified form ; the type of curve resembles that of toluene.
From the remaining curves it is evident that when groups of
stronger residual affinity, *e.g.* $>C=O$, $-NH_2$, $-NO_2$, are
inserted the benzene absorption is unrecognizable, being
replaced either by a broad band nearer the visible spectrum

(aniline, Fig. 26) or by general absorption (acetophenone, Fig. 26, and nitrobenzene, Fig. 27).

The influence of a group may be lessened by saturating it or by screening it from the benzene nucleus by the intervention of more saturated groups. The effect of saturation is illustrated by the absorption curve of aniline in presence of excess of hydrochloric acid.
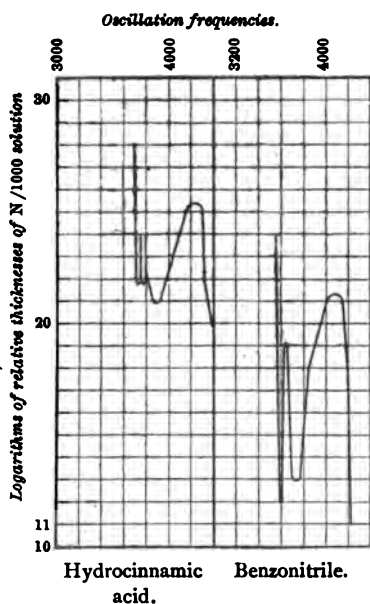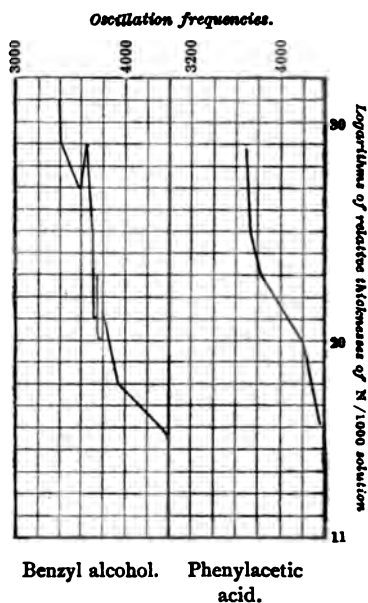
FIG. 28.   FIG. 29.

The change in the type of absorption curve on passing from aniline to the hydrochloride is remarkable; in the latter substance the benzene bands are clearly recognizable, and it is evident that the disturbance caused by the residual affinity of the amino group is lessened. It is difficult to find good illustrations of the screening effect of saturated groups; but perhaps the best is that afforded by phenylacetic (Fig. 29)

and hydrocinnamic acids (Fig. 28).   These substances are
represented by the formulæ

$$C_6H_5CH_2COOH \qquad C_6H_5CH_2CH_2COOH$$
Phenylacetic acid.   Hydrocinnamic acid.

With the former substance the single intervening methylene
group does not seem sufficient to prevent the mutual action of
the carboxyl and benzene nucleus; but when a second methy-
lene is inserted, as in hydrocinnamic acid, the benzene bands
make their appearance.   However, benzoic acid, in which the
carboxyl and benzene nucleus are directly united, behaves
differently from either of these substances . the absorption
curve shows a band[1] with its head at about 3600 units.   The
absorption curve of the unsaturated cinnamic[2] acid

$$C_6H_5CH=CHCOOH$$
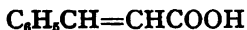
exhibits a broad band at about 3600 units.

It should be observed that the disturbance produced by
unsaturated groups on the benzene system may be detected
in a similar manner with refractive power and magnetic
rotation.

Sufficient data are not yet available to permit the discussion
of the effect of substitution in open chain systems of unsaturated
carbon, but the first steps in this direction have been taken by
Baly and Schaefer[2] in their study of benzene derivatives with
unsaturated side chains.   If in cinnamylidene acetone the
methyl group is replaced by the unsaturated hydroxyl—

$$C_6H_5CH=CH-CH=CH-CO-CH_3$$
Cinnamylidene acetone.

$$C_6H_5CH=CH-CH=CH-COOH$$
Cinnamylidene acetic acid.

it seems that the carbonyl group will then have less residual
affinity available for conjugation with the ethylenic system.
The result is that the absorption band is shifted towards the

---

[1] Hartley and Hedley, *Trans. Chem. Soc.*, **91**, 322 (1907).

[2] Baly and Schaefer, *Trans. Chem. Soc.*, **93**, 1812 (1908).

violet.   The positions of the heads of the absorption bands are
as follows—

			$1/\lambda$
Cinnamylidene acetone	.	. .	3100
„	„	acetic acid . .	3300
„	„	sodium salt	3450

B.—3. The Use of Absorption Spectra in determining the Constitution of Organic Compounds

§ 15. *GENERAL*

It now remains to consider the means by which absorption spectra have been turned to account in determining the constitution of compounds.   The method was devised by Hartley.   It consists in comparing the absorption curves of the substance whose constitution is sought with those of substances of known structure.   If the molecular absorption curves of one of these standard substances closely resembles that of the compound in question, it may be inferred that the structures of the two are similar.

Like other physical methods, this is particularly useful in cases where chemical evidence fails to give definite information, as with tautomeric compounds or other substances, whose structure may vary according to the reagent present, and with alkaloids of complex structure.   In some cases a mixture of two interchangeable forms may occur, and it is then possible roughly to estimate the amount of each by comparing the spectrum with those of artificial mixtures containing known amounts of each structural type.   We shall deal first with tautomeric substances, and then with compounds containing various types of labile structures.

§ 16. *SUBSTANCES CONTAINING THE* —NH—CO— *GROUP*

With the majority of compounds of this type there is some doubt whether the group exists in the

$$\text{Lactam —NH—CO—}$$
or $$\text{Lactim —N}=\text{C(OH)—}$$
arrangement.

Isatine was the first substance in which these alternative structures were discussed from the chemical point of view, and we may therefore deal with it in some detail.

1. *Isatine.*—Baeyer[1] showed that the silver salt of isatine interacts with ethyl iodide, forming an ethyl derivative which may be decomposed by potassium hydroxide into ethyl alcohol and potassium isatine; and the latter in turn can be prepared directly from isatine. Baeyer concluded that the ethyl group in this derivative is united to the isatine nucleus through the oxygen atom as in I.—
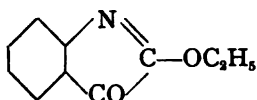
$$\underset{\text{Ethyl isatine.}}{\underset{\text{I.}}{\text{C—OC}_2\text{H}_5}} \qquad \underset{\substack{\text{Isatine (Baeyer).}\\ \text{II.}}}{\text{C . OH}}$$
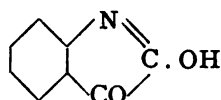
isatine itself having a corresponding structure (II.). Baeyer's view was afterwards confirmed by the work of Schunck and Marchlewski,[2] which proved that isatine can only give monoximes and mono-hydrazones. But Goldschmidt[3] had in the mean time found that isatine reacts with phenyl isocyanate, giving—

$$\text{CO—NH . C}_6\text{H}_5$$
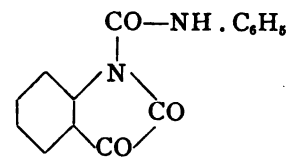
N-Carbanilidoisatine.

and not the carbamate

$$\text{C—OCO . NHC}_6\text{H}_5$$

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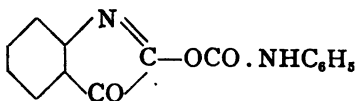
[1] Baeyer, *Ber.*, **15**, 2120 (1882); **16**, 1704 (1883).

[2] Schunck and Marchlewski, *Ber.*, **28**, 543, 2526 (1895); **29**, 194, 1030 (1896).

[3] Goldschmidt, *Ber.*, **23**, 278 (1890); Knorr, *Ann.*, **293**, 81 (1896).

which would be expected if isatine had the formula assigned
to it by Baeyer.   This fact points to the lactam formula.
We see, then, that from chemical facts alone it is impossible
to speak with any certainty as to the constitution of isatine.
But the lactim structure given by Baeyer to his ether has
never been called in question; in fact, it has been confirmed
by the discovery of an isomeric ether which can be proved
from its mode of formation to have the lactam structure.
This substance is obtained [1] by the oxidation of N-ethyl
indole (I.) or its carboxylic acid with sodium hypobromite.
An intermediate dibromo-product (II.) is formed, but this is
transformed by alkali into N-ethyl isatine (III.).

I.   II.   III.
N-ethyl indole.   Ethyl pseudoisatine.
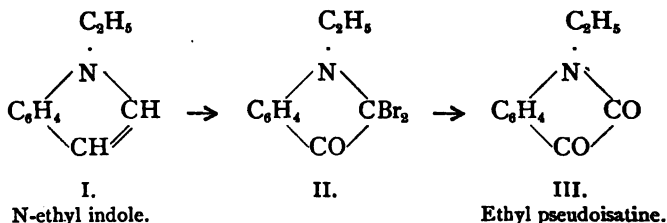
Hartley and Dobbie [2] were able to determine the constitu-
tion of isatine by comparing the absorption curve with those
of the N-methyl and O-methyl ethers.   The absorption curves
of the two ethers are entirely different; the former shows two
bands and the latter only one.   Since the curve for isatine
closely resembles that of the N-methyl ether, it follows that
the parent substance must exist in the lactam form.

Isatine.
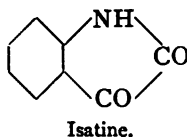
The structure of *carbostyril* has been elucidated in the same

[1] Fischer and Hess, *Ber.*, 17, 563 (1884); Baeyer, *Ber.*, 16, 2193
(1883).
[2] Hartley and Dobbie, *Trans. Chem. Soc.*, 77, 640 (1899).

manner. Friedländer,[1] having studied the reactions by which this substance is formed, summed up in favour of the lactim or hydroxy-quinoline structure (I.), the alternative lactam formula being the quinolone (II.).

$$C_6H_4 \diagup \substack{CH=CH \\ | \\ N=C.OH}$$
I.

$$C_6H_4 \diagup \substack{CH=CH \\ | \\ NH-CO}$$
II.
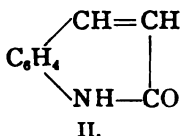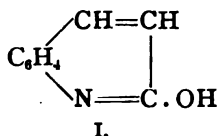
But Hartley and Dobbie,[2] on comparing the absorption curves of carbostyril with those of the two methyl ethers,—

$$C_6H_4 \diagup \substack{CH=CH \\ | \\ N=C.OCH_3}$$
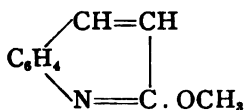
O-Methyl carbostyril.

$$C_6H_4 \diagup \substack{CH=CH \\ | \\ N \quad -CO \\ | \\ CH_3}$$
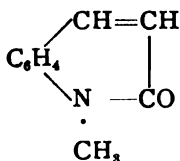
Methyl pseudocarbostyril.

found that it is almost identical with that of the N-methyl derivative. Hence carbostyril must have the lactam structure (II.).

The chemical behaviour of *oxycarbanil* (I.) seems to show[3] the presence of the lactam structure, and this is confirmed[4] by the absorption spectrum, which is similar to that of the lactam ether (II.)—

$$C_6H_4 \substack{\diagup O \diagdown \\ \quad\quad CO \\ \diagdown NH \diagup}$$

Oxycarbanil.
I.

$$C_6H_4 \substack{\diagup O \diagdown \\ \quad\quad CO \\ \diagdown N \diagup \\ \quad C_2H_5}$$
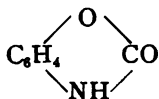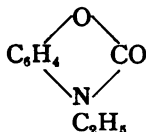
N-ethyl oxycarbanil.
II.

[1] Friedländer, *Ber.*, **15**, 337 (1885).
[2] Hartley and Dobbie, *Trans. Chem. Soc.*, **75**, 640 (1899).
[3] Bender, *Ber.*, **19**, 2269, 2952 (1886).
[4] Hartley, Dobbie and Paliatseas, *Trans. Chem. Soc.*, **77**, 839 (1900).

The method followed by Baly and Baker [1] in determining the constitution of the *oxypyridines* depends on the behaviour of the absorption bands under the influence of acids and alkalies, and it is thus somewhat different from that adopted in the foregoing cases.   Generally speaking, most pyridine derivatives have a single well-defined band in the ultra-violet. With derivatives containing the true pyridine structure (I.)—

Pyridine.
I.
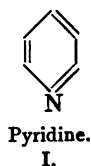
β-Oxypyridine.
II.

the addition of acids causes the persistence of the band to increase.   Since the band of β oxypyridine behaves in this manner, Baly and Baker consider that the substance is a true pyridine derivative (II.).   Moreover, the phenolic character of the substance is confirmed by the addition of alkali, which causes the band to shift towards the red without affecting its persistence ; this is characteristic [2] of the phenols.   The α and γ oxypyridines evidently have the pyridone structures (I. and II.)—

α-Pyridone.

I.

N-methyl
α-pyridone.

Iᴀ.

γ-Pyridone.

II.

Phorone.

IIᴀ.
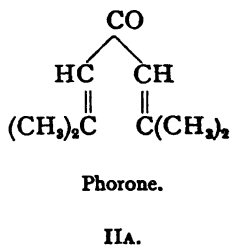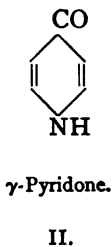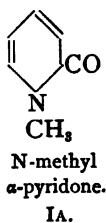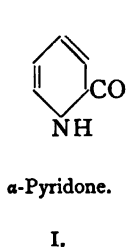
for with the α compound the persistence of the band is not altered, and with the γ compound it is actually lessened by the addition of acids.   Moreover, the absorption curves of the two substances show a striking similarity to those of their structural

[1] Baly and Baker, *Trans. Chem. Soc.*, **91**, 1122 (1907).
[2] Baly and Ewbank, *Trans. Chem. Soc.*, **87**, 1347 (1905).

analogues : N-methyl α-pyridone (IA.), and phorone (IIA.) respectively. So far as β oxypyridine is concerned, the result is entirely in harmony with chemical facts. But the reactions of α and γ oxypyridines are confusing,[1] so that this spectroscopic evidence is of especial value.

In concluding the study of this group[2] of compounds, we may notice that Wislicenus and Koerber[3] have found it possible directly to convert lactim into lactam ethers by the action of heat. Thus methoxy caffeine may be transformed into tetramethyluric acid—

| Methoxycaffeine. | Tetramethyl uric acid. |
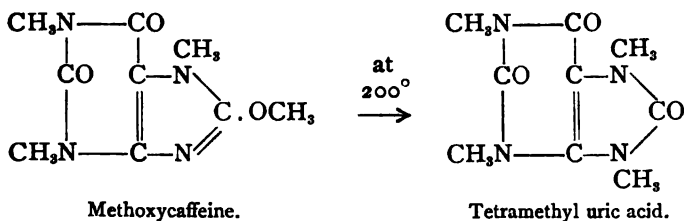
Hartley[4] claims to have found evidence for the reverse change, since the ill-defined absorption bands of the lactam ethers, caffeine and theobromine, become definite on keeping or boiling the solutions.

It should be observed that the results obtained from the spectroscopic examination of these imino compounds uniformly show that the parent substances exist in the lactam condition.

§ 17. *COMPOUNDS CONTAINING THE* —CH₂—CO—
GROUP

This important group of compounds has been very thoroughly studied by Stewart and Baly and by Lowry and Desch, and the results attained by these experimenters have

[1] See von Pechmann and Balzer, *Ber.*, **24**, 3144 (1891).

[2] For other cases see Hartley, Dobbie and Lauder, *Brit. Assoc. Report*, 1901, and Hartley, *Trans. Chem. Soc.*, **87**, 1796 (1905).

[3] Wislicenus and Koerber, *Ber.*, **35**, 1991 (1902).

[4] Hartley, *Trans. Chem. Soc.*, **87**, 1818 (1905).

been already discussed. But previously to these attempts to discover the cause of absorption in this class of substance, Hartley and Dobbie had employed the method of comparison in examining the relations between certain isomeric forms of these compounds.

The investigations of Knorr[1] on *dibenzoyl succinic ester* showed that this compound exists in three isomeric forms. When iodine interacts with the sodium compound of benzoyl-acetic ester—

$$C_6H_5COCHNaCOOC_2H_5 \atop C_6H_5COCHNaCOOC_2H_5 + 2I = {C_6H_5CO-CH-COOC_2H_5 \atop | \atop C_6H_5CO-CH-COOC_2H_5} + 2NaI$$
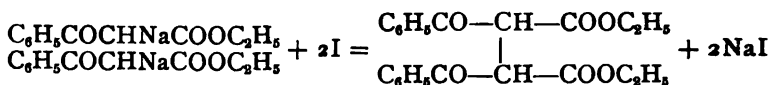
two of the isomerides are produced. From their insolubility in dilute alkalies and from the negative results of the ferric chloride test, Knorr inferred that these have the ketonic structure, and accordingly must be stereoisomerides. The more easily fusible would be the *meso*-compound, and the other would be the racemic ester.

γ or *meso*-dibenzoylsuccinic ester, m.p. 75°.
β or racemic dibenzoylsuccinic ester, m.p. 128–30°.

By acidifying the ice-cold solution of the sodium salt, Knorr obtained the third isomeric ester as a greenish-yellow oil. This compound shows the reactions of the enolic structure, and when heated it is converted into a mixture of the ketonic esters. Knorr formulated this substance as

$$C_6H_5C=CH-COOC_2H_5 \atop OH \;| \atop C_6H_5C=CH-COOC_2H_5 \atop OH$$
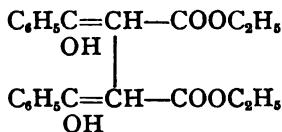
α Dibenzoylsuccinic ester (liquid).

The relations between the spectra of these compounds confirm[2] the results of chemical experience. Thus the

[1] Knorr, *Ann.*, 293, 70 (1896); 306, 85 (1898).
[2] Hartley and Dobbie, *Trans. Chem. Soc.*, 77, 498 (1900).

absorption curves of the β and γ isomerides are identical with one another but different from that of the α compound. Moreover, the change of the α to the β and γ forms can be followed by examining a solution of the α ester at intervals after preparation. After the discoveries of Baly and Desch, it might be supposed that these esters consist of equilibrium mixtures of the ketonic and enolic forms, since each substance gives a band in the ultra violet. But the presence of the benzene nuclei invalidates any such conclusion; in fact, for the same reason the spectra alone can afford no clue to the structure of these compounds. However, the relations between them are clearly demonstrated. Also the spectrum of *phloroglucine* has been studied with the aid of the spectroscope. This substance behaves with some reagents as though it had the phenolic structure (I.) and with others according to the ketonic formula (II.).

$$\underset{\text{I.}}{\text{OH} \overset{\displaystyle\bigcirc}{} \text{OH, OH}} \qquad \underset{\text{II.}}{\text{CH}_2 \overset{\displaystyle\bigcirc}{} \text{CO, CH}_2, \text{CO}} \qquad \underset{\text{III.}}{\text{CH}_3\text{O} \overset{\displaystyle\bigcirc}{} \text{OCH}_3, \text{OCH}_3}$$
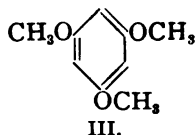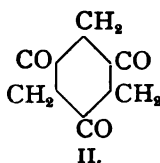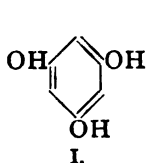
But since phloroglucine gives a spectrum [1] almost identical with that of its tri-alkyl ether (III.) it must be regarded as a true phenol. Also it is probable that pyrogallol is a phenol, for the spectrum resembles that of phloroglucine.

We shall now turn to certain aromatic compounds such as nitro- and nitroso-phenol in which the benzene system is labile and may undergo rearrangement to the quinonoid structure.

§ 18. COMPOUNDS CONTAINING A LABILE BENZENE SYSTEM

Perhaps the *nitrophenols* are the most widely known examples of this type of substance. On account of the marked deepening of colour produced by converting the ortho and para derivatives to their alkali salts, Armstrong suspected that the

---

[1] Hartley, Dobbie and Lauder, *Trans. Chem. Soc.*, **81**, 929 (1902).

benzenoid structure of the free compounds is changed on salt formation to the quinonoid. Hantzsch then confirmed this

Full curve = *p. Nitro-phenol in neutral solution*
Dash curve = *p. Nitro-anisole*
Dot-dash curve = *p. Nitro-phenol in alkaline solution*
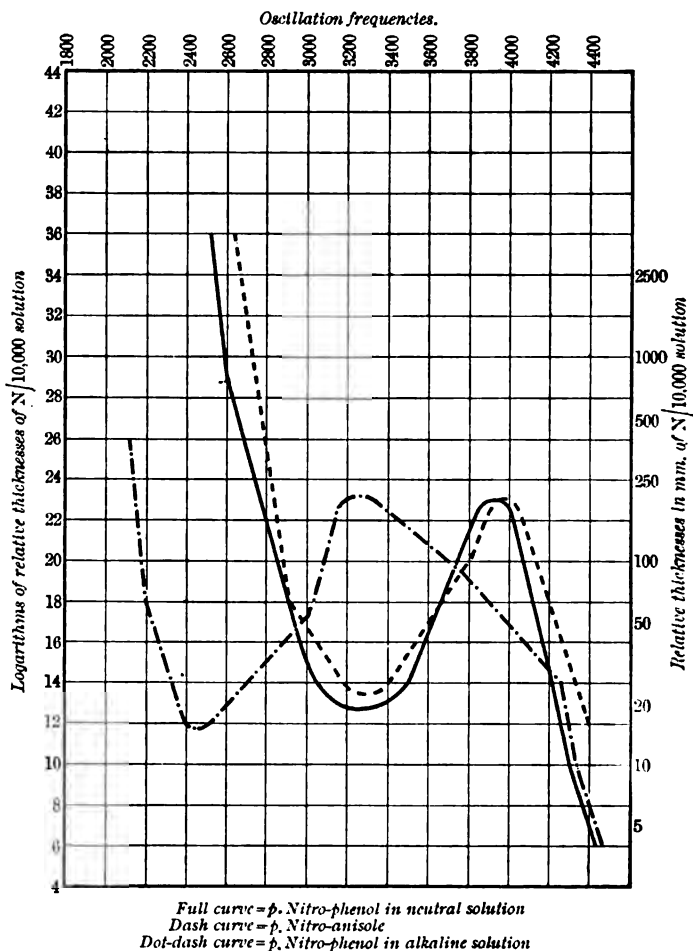
FIG. 30.

by isolating the "chromo" series of esters. The spectra of these compounds have been studied by Baly, Edwards and

Stewart.[1]   The very close resemblance between the curves
of   *p*-nitroanisole   and   *p*-nitrophenol   in   neutral   solution
shows that the latter has the benzenoid structure.   But on
adding alkali to the solution of the phenol the absorption
spectrum entirely alters, whence it may be inferred that the
structure of the substance has changed.   Moreover, the new
band is similar to that present in the quinones.   A similar
change of spectrum was observed with *o.* nitrophenol and in a
lesser   degree   with   the   *meta* derivative.   According   to   Baly,
Edwards, and Stewart, the existence of *meta* quinones is thus
demonstrated.[2]   The case of *para*-nitrophenol is illustrated by
the accompanying figure.

   The same investigators have concluded[3] that free *para*-
nitrosophenol is a true nitroso-compound (I.) since the absorp-
tion curve is similar to that of nitrosobenzene (II.).

OH   O

NO   NO   N . ONa
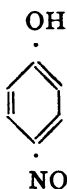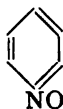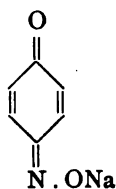
I.   II.   III.

Moreover, when alkali is added to the solution the spectrum
becomes entirely different, so that we may infer that the salt
exists in the quinone monoxime form (III.).   However, the con-
stitution of *p*-nitrosophenol cannot be regarded as definitely
settled.   It is remarkable that chemical data seem to show the
reverse relations[4]: that the free substance is the quinone
monoxime and the salt is the nitroso compound.   Moreover,

   [1] Baly, Edwards and Stewart, *Trans. Chem. Soc.*, **89**, 518 (1906).   Very
recently one of these authors has continued the study of the nitrophenols
and amines (*Trans. Chem. Soc.*, March, 1910), and it is concluded that the
salts of these compounds do not contain the quinonoid arrangement.
   [2] See p. 386 ; also Hantzsch, *Ber.*, **40**, 330 (1907).
   [3] See also Hartley, *Trans. Chem. Soc.*, **85**, 1017 (1904).
   [4] *Ber.*, **32**, 3034 (1899).

Hartley[1] finds that the spectrum of *p.* nitroso-dimethylaniline has no resemblance to that of *p.* nitrosophenol, and the difference cannot be accounted for by the replacement of $N(CH_3)_2$ for OH. There should, however, be no difficulty in deciding the question, since the two isomeric ethers

are now available. The former is produced by oxidation of *p*-anisidine with Caro's reagent, and the latter by methylation of the nitrosophenol.

Absorption spectra have been employed by Tuck[2] and by Hewitt[3] in studying the interesting question of the constitution of the *hydroxyazo compounds*. Since it is difficult to decide from chemical behaviour whether these substances have the azo (I.) or the quinonoid (II) structures,
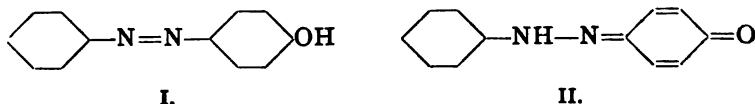
Tuck compared their absorption spectra with those of their ethers and acyl derivatives. These substances, which served as standards of comparison, have been shown[4] to have the azo structure :
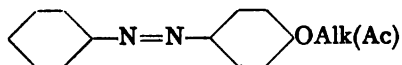
[1] Hartley, *Trans. Chem. Soc.*, **85**, 1016 (1904) ; *Brit. Assoc. Report*, 107, 1904.

[2] Tuck, *Trans. Chem. Soc.*, **91**, 449 (1907).

[3] Hewitt and Thomas, *Trans. Chem. Soc.*, **95**, 1292 (1909).

[4] Jacobsen and Fischer, *Ber.*, **25**, 995 (1892); see also Auwers and Eckhardt, *Ann.*, **309**, 336 (1908).

It was found that the *para* hydroxy derivatives : benzene azo-phenol and benzene azo-*m*-cresol, have the same spectra as the alkyl ethers, whence it is clear that the two classes of substance have the same constitution. Moreover, the characteristic portion of the curve closely resembles that of azo-benzene.[1] The azo structure (I.) of the *para* hydroxy compounds is thus established.   Examination of the *ortho* derivatives :
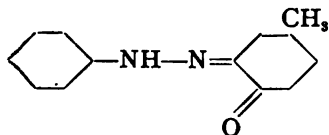
Benzene-azo *p*. cresol.   *p*. Toluene-azo *p*. cresol.
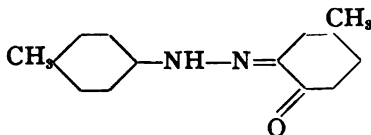
showed them to have the quinonoid constitution, for their spectra are entirely different from those of the alkyl ethers, *e.g.*
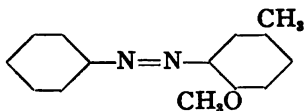
Benzene-azo *p*. cresetol.

which in turn resemble azo-benzene and the ethers of the *para* compounds.   It should be observed that the acyl derivatives of the *ortho* compounds appear to have the quinonoid structure, *e.g.*
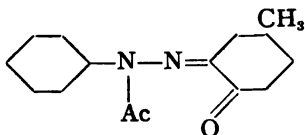
since their absorption spectra are similar to those of the parent compounds.   The spectra of the hydrochlorides of the *p*. azo-phenols and their ethers profoundly differ from those of the parent compounds, and it is therefore evident that a change in structure takes place in the formation of these salts.   Moreover,

[1] Baly and Tuck, *Trans. Chem. Soc.*, **89**, 985 (1906).

since the hydrochlorides of the ethers and of the phenols give identical spectra, the usual quinone-hydrazone structure

$$C_6H_4NH—N=C_6H_4=O$$
$$\wedge$$
$$HCl$$
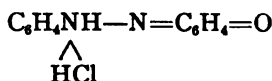
for these salts must be abandoned. Hewitt,[1] taking into account the chemical behaviour of these compounds, sums up in favour of an oxonium structure. The salt formation would then be represented by the following equation—

$$C_6H_4N=N—C_6H_4OH(C_2H_5) + HCl$$
$$= C_6H_4—NH—N=C_6H_4=O\underset{Cl}{\overset{H \text{ or } (C_2H_5)}{<}}$$
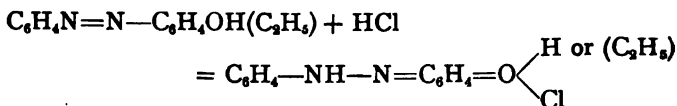
§ 19. *THE RELATION BETWEEN THE HYDRAZONE AND AZO STRUCTURES*

E. Fischer,[2] during his researches on the phenyl hydrazones of the aldehydes, found that benzene azoethane may be converted by mineral acids or sodium ethylate into the isomeric acetaldehydephenylhydrazone—

$$C_6H_5N=N . CH_2—CH_3 \quad \rightarrow \quad C_6H_5NH—N=CH—CH_3$$
Benzeneazoethane.   Aldehydephenylhydrazone.
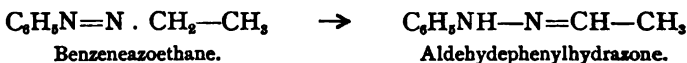
Somewhat later Chattaway[3] suspected a change of the reverse nature in the action of light on benzaldehydephenyl-hydrazone, which is transformed into the corresponding azo compound. These facts induced Baly and his co-workers[4] to examine the absorption spectra of a series of hydrazones and osazones in order to obtain more complete information of the

[1] Fox and Hewitt, *Trans. Chem. Soc.*, **93**, 333 (1908); Hewitt and Thomas, *ibid.*, **95**, 1292 (1909); Hewitt and Pope, *Ber.*, **30**, 1624 (1897); see also Hantzsch, *Ber.*, **42**, 2129 (1909).

[2] Fischer, *Ber*, **29**, 794 (1896); **36**, 56 (1903).

[3] Chattaway, *Trans. Chem. Soc.*, **89**, 462 (1906).

[4] Baly and Tuck, *Trans. Chem. Soc.*, **89**, 982 (1906); Baly, Tuck, Marsden and Gazdar, *Trans. Chem. Soc.*, **91**, 1572 (1907).

conditions governing the reaction. The isomeric change produced by the action of light on the aldehyde hydrazones

Oscillation frequencies.
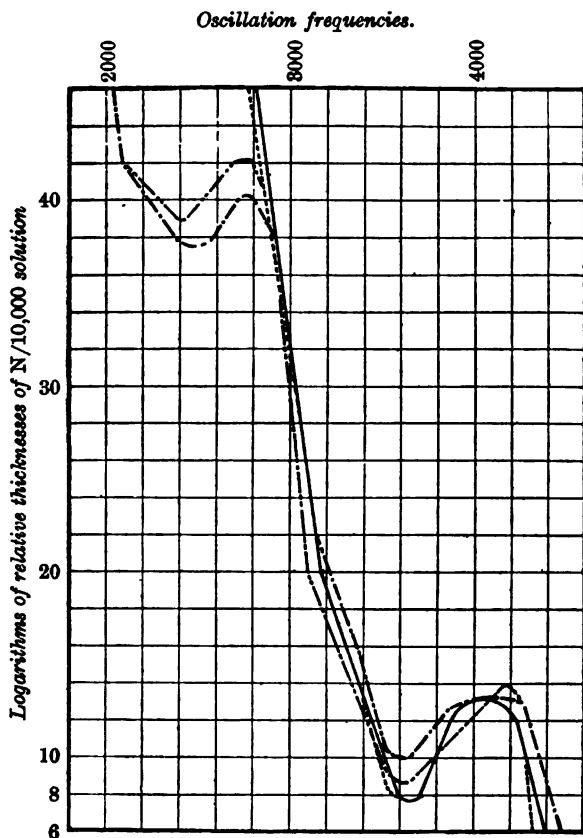
FIG. 31.

Full curve = Acetaldehydephenylhydrazone in acetic acid.
Dot-and-dash curve = Acetaldehydephenylhydrazone after exposure to light.
Dotted curve = Acetaldehydephenylmethylhydrazone.
Dash-and-two-dots curve = Acetaldehyde *p*-bromophenylhydrazone.

is accompanied by the appearance of a well-marked band in the visible region of the spectrum. In fact, the colourless

solutions of the hydrazones on exposure to sunlight rapidly become deep yellow. The accompanying illustration of the curves obtained from acetaldehyde phenylhydrazone serves to show the change in the absorption. The full and dot-dash curves were respectively obtained before and after exposure to light.

According to the accepted explanation, the reaction may be represented as follows :—

$$C_6H_5NHN{=}CH.CH_3 \quad \rightarrow \quad C_6H_5{-}N{=}N{-}CH_2.CH_3$$

and evidently it depends on the mobility of the remaining hydrogen atoms of the hydrazine group. Replacement of the hydrogen atom by methyl should inhibit the reaction. This explanation is confirmed by the behaviour of the methyl phenyl hydrazone of acetaldehyde

$$C_6H_5N{-}N{=}CH{-}CH_3$$
$$|$$
$$CH_3$$
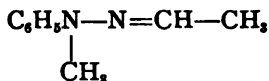
Since the spectrum of this substance is identical with that of the unsubstituted phenylhydrazone, it is clear that the latter has the true hydrazone structure. Moreover, there is no change of spectrum when the methyl derivative is exposed to sunlight. It may be observed that there is no proof whether the change of hydrazo to azo compound is complete in the dilute solutions examined. Reference to the foregoing illustration will show that the spectra of the exposed solution gives the characteristic band of the hydrazone, but with rather less persistence than the pure substance. Probably an equilibrium between the two forms is attained.

By using different solvents it may be shown that the change of hydrazo to azo structure is retarded by the presence of acids, a fact which entirely conforms with the observation of Fischer in the case of benzeneazoethane.

The nature of the groups attached to the hydrazine and to the ketonic group of the original aldehyde influences the reaction. The hydrazones of *p*. bromophenylhydrazine— $Br.C_6H_4.NH.NH_2$—change more slowly than the parent

compounds. Substitution of the aldehydic hydrogen by alkyl seems to be without effect; but if the alkyl group is replaced by phenyl, as in benzaldehydephenylhydrazone, the change cannot be detected in solution, but only in the solid state.

It is remarkable that with the phenyl hydrazones of the α hydroxy-ketones, such as

$$C_6H_5 . C . CH_2OH \qquad C_6H_5 . C . CHOHC_6H_5$$
$$N . NHC_6H_5 \qquad N . NHC_6H_5$$

the change to the azo form takes place very slowly. With these substances the change requires two or three days, whereas in normal cases it is complete in about three hours or even less. Baly considers that the retardation is due to the mutual influence of the unsaturated hydroxyl and the adjacent double linkage, and the condition which is thus set up in the carbinol group may account for the ease with which this is oxidised.

§ 20. *PSEUDO-AMMONIUM BASES*

The substituted ammonium salts of halogen acids may be converted into the corresponding hydroxides by the action of silver hydroxide. The majority of these ammonium bases are stable substances; they are readily soluble in water, and their solutions, which are strongly alkaline to litmus, have a conductivity of the same order as those of the common alkali hydroxides. There are, however, some salts of the ammonium type which yield with silver oxide neutral substances of sparing solubility. From their neutral character it is clear that the products of these abnormal reactions cannot be true ammonium bases, and it has been generally assumed that their hydroxyl group is attached to carbon. Hantzsch[1] investigated the course of these reactions by determining the conductivity of the liquid at intervals after the decomposition with silver hydroxide. In a few cases it was found that immediately after the decomposition the conductivity approximated to that expected for the true ammonium base; but after lapse of time the value fell to zero, the solution becoming neutral. It is therefore evident that

[1] Hantzsch, *Ber.*, **32**, 575, 2201, 3109, 3675 (1899).

the true ammonium base is first produced, and that it subsequently undergoes transformation to the neutral form. Hantzsch therefore terms the latter substance the " pseudo-ammonium base."

In the case of phenylacridine methiodide the reaction may be represented as follows :—

C_6H_5
C
C_6H_4 | C_6H_4
N
CH_3 I

⟶ Alkali.

C_6H_5
C
C_6H_4 | C_6H_4
N
CH_3 OH
Acids.

⟶ Rearrangement.

C_6H_5
C(OH)
C_6H_4 C_6H_4
N
·
CH_3

Phenyl acridine methiodide. Intermediate ammonium base not isolable. N. Methyl phenyl-acridol.
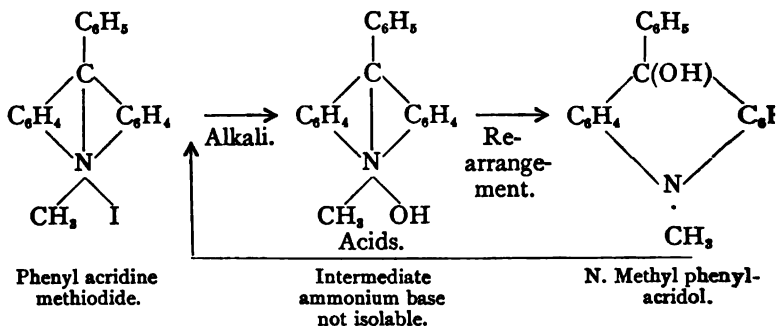
the pseudo-base—N. methyl phenyl-acridol—being formed from the ammonium base by migration of hydroxyl. It is difficult to obtain direct chemical evidence for this structure of the pseudo-base, since acids effect the reverse change to the ammonium salt. But Dobbie and Tinkler [1] have decided the question by comparing the spectra of the members of the acridine group.

The absorption curve of phenylacridine methiodide, which shows two bands with heads at 2400 and 2800 units, is entirely different from that of dihydrophenyl acridine, which has only one band with head at 3400 units. Moreover, the very close resemblance between the curves of the pseudo-base and the dihydroacridine (see Fig. 33)

C_6H_5
·
CH
C_6H_4 C_6H_4
NH
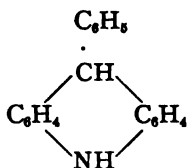
conclusively proves the structure assigned to the former.

[1] Dobbie and Tinkler, *Trans. Chem. Soc.*, **87**, 269 (1905) ; Tinkler, *Trans. Chem. Soc.*, **89**, 856 (1908).

Dobbie and Tinkler were able further to show that in alcohol the pseudo-base tends to assume the ammonium structure, since in that solvent the curve approximates to that of the methiodide. The absorption curve given by an alcoholic
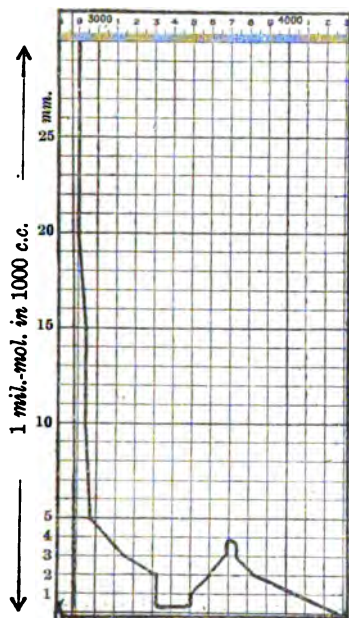
Phenylmethyl acridol in ether or chloroform.

FIG. 32.
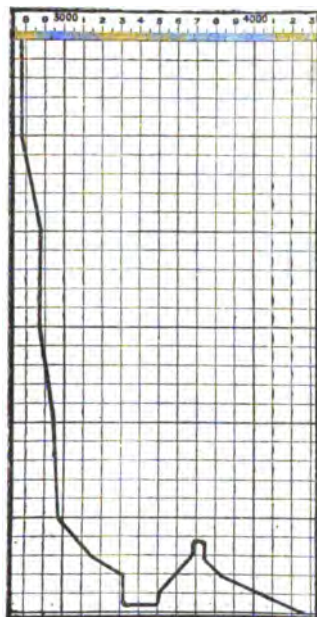
Dihydrophenyl acridine.

FIG. 33.

solution is identical with that yielded by a mixture of 75 per cent. dihydrophenylacridine and 25 per cent. methiodide.

The researches dealing with the reactions and decomposition of *cotarnine* have elucidated the main structure of that substance, and the discussion has been narrowed down to the choice between three alternative formulæ. All chemists are agreed that the salts of cotarnine should be represented as derivatives of the ammonium type (I.).

$$\text{*}C_8H_6O_3 \underset{\diagdown CH_2-CH_2}{\overset{\diagup CH=N(CH_3)OH}{\bigg|}}$$

I.

$$C_8H_6O_3 \underset{\diagdown CH_2-CH_2}{\overset{\diagup CHO.HN.CH_3}{\bigg|}}$$

II.

$$C_8H_6O_3 \underset{\diagdown CH_2-CH_2}{\overset{\diagup CH(OH)-N.CH_3}{\bigg|}}$$

III.
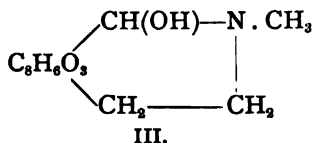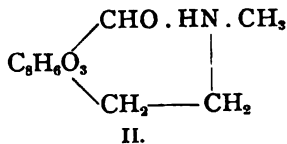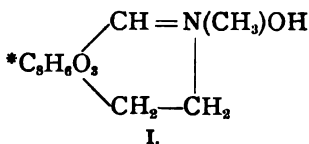
According to Roser,[1] cotarnine, which is liberated by treating these salts with alkali, should be represented as an aldehyde and secondary base (II.); whilst Decker[2] advocates the structure of a carbinol derived from isoquinoline (III.). According to either alternative, cotarnine appears to be a pseudo-base, and this induced Hantzsch[3] to study the conductivity phenomena which accompany the liberation of cotarnine from its salts. But the results only added further confusion, for they seem to indicate that, after being liberated in solution, the base exists as an equilibrium mixture of the ammonium form, the carbinol and perhaps also the aldehyde base. The application[4] of the spectrographic method to this problem was attended with brilliant success. Dobbie and his co-workers chose substances whose spectra should serve as comparison standards for either structure. The spectrum of the chloride of the base was taken as representing the ammonium structure and those of hydrocotarnine and cyanhydrocotarnine as typical of the carbinol structure.

* The residue $C_8H_6O_3 <$ represents the group
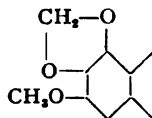
[1] Roser, *Ann.*, **249**, 156, 168 (1888) ; **254**, 334, 359 (1889).
[2] Decker, *Journ. für Pr. Chem.*, **47**, 222 (1893).
[3] Hantzsch and Kalb, *Ber.*, **32**, 3109 (1899).
[4] Dobbie, Lauder and Tinkler, *Trans. Chem. Soc.*, **85**, 598 (1903).

$$\text{C}_8\text{H}_6\text{O}_3 \underset{\diagdown \text{CH}_2-\text{CH}_2}{\overset{\diagup \text{CH}=\text{N}(\text{CH}_3)\text{Cl}}{<}}$$

Cotarnine chloride.

$$\text{C}_8\text{H}_6\text{O}_3 \underset{\diagdown \text{CH}_2-\text{CH}_2}{\overset{\diagup \text{CH}_2-\text{N}\,.\,\text{CH}_3}{<}}$$

Hydrocotarnine.

$$\text{C}_8\text{H}_6\text{O}_3 \underset{\diagdown \text{CH}_2-\!-\!-\!-\text{CH}_2}{\overset{\diagup \text{CH}(\text{CN})-\text{N}\,.\,\text{CH}_3}{<}}$$
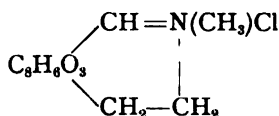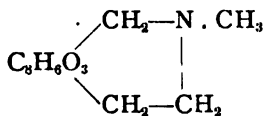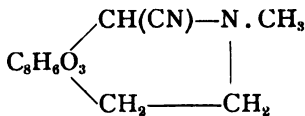
Cyanhydrocotarnine.

· There is no doubt as to the correctness of the formulæ assigned to these compounds. Fortunately the spectra of these two classes of compounds are very different from one another. The spectrum of cotarnine chloride exhibits two well-marked absorption bands, one of which is near the visible region; the middle of these bands occurs at λ 3278 and λ 2500. All derivatives giving this spectrum are yellow. The spectrum of hydrocotarnine has only one band, and this is situated at about λ 2857. Since all the derivatives of cotarnine examined give spectra conforming to one or other of these types, it appears that the aldehydic formula of Roser must be discarded.

The behaviour of cotarnine recalls that of the acridonium base described in a previous paragraph; the structure varies from the carbinol to the ammonium type according to the solvent employed. The spectra of ethereal or chloroform solutions show that the base is present as the carbinol form, whilst alcoholic solutions seem to contain a mixture which becomes richer in ammonium base when kept or diluted. When alcohol is added to a solution of cotarnine in ether, the carbinol changes to the ammonium base, the amount of the latter increasing with the quantity of alcohol present. It is possible to estimate the proportions of each form in these mixtures by comparing their spectra with those of solutions containing known amounts of chloride and cyanhydrocotarnine. In this way the effect of adding alcohol to a carbinol solution of cotarnine may be quantitatively studied. The following

data were obtained by adding methyl alcohol to an ethereal solution of the base at ordinary temperatures.

TABLE VIII.

Per cent. CH$_3$OH.	Per cent. carbinol.	Per cent. ammonium base.
0	100	—
25	97·5	2·5
40	92·5	7·5
50	85·0	15·0
100	75·0	25·0

The change of carbinol to ammonium base is favoured not only by the presence of hydroxylic solvents, such as water and alcohol, but also by diluting the solutions in these media, by lapse of time after the solutions have been prepared, or by rise of temperature. As might be expected, the reverse process—the change of ammonium base to carbinol—is induced by alkali hydroxide, and the amount of carbinol present increases with the concentration of the alkali. The following table shows the data obtained on adding sodium hydroxide to an aqueous solution of cotarnine at the ordinary temperature.

TABLE IX.

TEMPERATURE 12°.

Strength of base.		Percentage of carbinol.	
		NaOH.	NH$_4$OH.
N		98·5	45
N/2		97	40
N/4		94	—
N/8		91	—
N/10		89	20
N/32		77·5	—
N/50		70	10
N/100		52·5	—
N/600		20	—

The right-hand column of the table contains the data obtained with ammonia solutions of corresponding strengths, and it will be observed that the weaker base has the slighter influence. Dobbie, Lauder and Tinkler[1] have suggested that this behaviour of cotarnine in presence of hydroxyl ions should be adapted to determining the relative strengths of bases. When acids are added to solutions of the carbinol, cotarnine salts of the ammonium type are found.

Dobbie and Tinkler[2] extended the study of pseudo-bases to hydrastinine, a derivative of the alkaloid hydrastine. The structure of hydrastine resembles that of cotarnine, in fact, the sole difference between them is that the former lacks the methoxyl group. The relations between the spectra of hydrastine derivatives show that the base behaves like cotarnine, the carbinol form (I.) and the ammonium form (II.) being interconvertible by the selective action of solvents.

$$C_7H_4O_2 \underset{CHOH-N.CH_3}{\overset{}{\diagup}} \underset{CH_3 \text{---} CH_2}{\overset{}{\diagdown}} \quad \underset{\longrightarrow}{\overset{\longleftarrow}{}} \quad C_7H_4O_2 \underset{CH_2-CH_2}{\overset{}{\diagup}} \underset{}{\overset{CH=N \diagup CH_3 \diagdown OH}{}}$$

Hydrastinine.

I. Carbinol form.   II. Ammonium form.
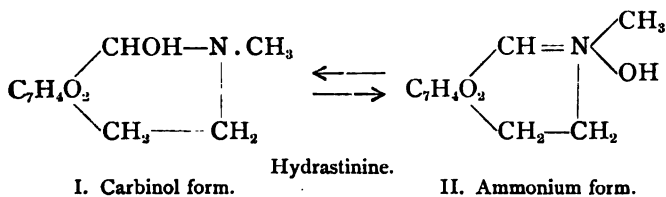
There is no doubt that in these researches dealing with pseudo-bases, Hartley's method is seen at the highest state of development to which it has yet been brought. No other physical property can be employed to determine the structure of such complex substances; in fact, it should be observed that the spectrographic method can be applied only to complex substances, for it is these which have the more characteristic spectra. Since most simple compounds have only general absorption or perhaps weak selective spectra, the characteristics of the alternative types cannot be sharply distinguished.

[1] Dobbie, Lauder and Tinkler, *Trans. Chem. Soc.*, **85**, 121 (1904).
[2] Dobbie and Tinkler, *Trans. Chem. Soc.*, **85**, 1004 (1904).

The peculiar advantages of absorption spectra were recognized by Hartley [1] at the outset of his investigations, when he recommended that the property should be used for identifying the alkaloids. Dobbie and Lauder [2] made practical use of this suggestion in studying the constitution of the alkaloids corydaline and berberine. Undoubtedly the most interesting application of the property in this field is the case of laudanine, $C_{20}H_{25}O_4N$, and laudanosine, $C_{21}H_{27}O_4N$, two rare alkaloids occurring in opium. Dobbie and Lauder [3] found that the absorption curves of these alkaloids are almost identical, thereby confirming the opinion of Hesse [4] that they are homologous.

At the same time Dobbie and Lauder were struck by the very close resemblance between the spectra of laudanosine and those of tetrahydropapaverine and corydaline, and although at the time nothing was known of the structure of laudanosine, they urged that this substance must be of similar constitution to the other two alkaloids. Very recently the prediction has been confirmed by synthesis, [5] which shows laudanosine to be N. methyl tetrahydropapaverine.

Beyond these typical examples, many other interesting problems have been solved with the help of absorption spectra. The following list is given for the convenience of those who wish to pursue the subject further.

The structure of diazo compounds. [6]

The structure of carbonium salts. [7]

Isonitroso compounds. [8]

Nitroso compounds. [9]

Perhalogen salts. [10]

[1] Hartley, *Phil. Trans.*, 471 (1885).

[2] Dobbie and Lauder, *Trans. Chem. Soc.*, **83**, 606 (1903).

[3] Dobbie and Lauder, *ibid.*, p. 626.

[4] Hesse, *Ann.*, **77**, 47 (1870).

[5] Pictet, *Ber.*, **42**, 1979 (1909).

[6] Dobbie and Tinkler, *Trans. Chem. Soc.*, **87**, 274 (1905).

[7] Baker, *ibid.*, **91**, 1490 (1907).

[8] Baly, Marsden and Stewart, *ibid.*, **89**, 966 (1906).

[9] Baly and Desch, *ibid.*, **93**, 1747 (1908).

[10] Tinkler, *ibid.*, **91**, 997 (1907); **93**, 1611 (1908).

Acid salts of aromatic azo compounds.[1]

Amino aldehydes and ketones.[2]

Polynitro compounds.[3]

Pyrones.[4]

Naphthacene quinones.[5]

Complex hydrocarbons obtained from naphthalene.[6]

The bearing of absorption spectra on the state of salts in solution has been very fully discussed by Rudorf.[7]

[1] Hewitt, *Trans. Chem. Soc.*, 95 (1909) ; Hantzsch, *Ber.*, **42**, 2129 (1909).

[2] Baly and Marsden, *Trans. Chem. Soc.*, **93**, 2108 (1908).

[3] Hantzsch and Picton, *Ber.*, **42**, 2119 (1909).

[4] Baly, Collie and Watson, *Trans. Chem. Soc.*, **95**, 144 (1909).

[5] Baly and Tuck, *Trans. Chem. Soc.*, **91**, 426 (1907).

[6] Homer and Purvis, *ibid.*, **93**, 1301 (1908).

[7] Rudorf, *Jahrbuch der Radioaktivität und Elektronik*, **3**, 422 (1907) ; **4**, 380 (1907) ; see also Baly, *Trans. Chem. Soc.*, **95** (1909).

CHAPTER XII

FLUORESCENCE

§ 1. *INTRODUCTION*

Many bodies, when examined by reflected light, show at their bounding surface a characteristic colour which is distinct from that produced by absorption. The first recorded observation of this phenomenon was in 1570,[1] but it was not until the nineteenth century that any attempt at a complete explanation was made. In 1845, Herschel[2] and Brewster[3] performed many important experiments on the nature and origin of the emitted light; Brewster arrived at the conclusion that it was due to internal dispersion, and he assumed that the incident and emitted light have the same wave length. The observation of Herschel that, if the exciting ray be polarized the emitted light is unpolarized, forms strong evidence against Brewster's explanation; but the theory seems to have been generally accepted until Stokes published his classical work on the subject.[4] Stokes gave to the phenomenon the name fluorescence. It was found that the fluorescent light is independent of the exciting light; Stokes confirmed Herschel's observation that polarization of the incident ray was not preserved in the emitted light, and he further showed that the incident and emitted rays are of different wave length.

Without following the historical development of the subject

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[1] See Kayser, *Handbuch der Spektroscopie*, vol. iv. 843 (1908).
[2] *Phil. Trans.*, 143 (1845).
[3] *Trans. Edin. Roy. Soc.*, 16, II. 111 (1846).
[4] *Phil. Trans.*, 143, II. 479 (1852); III. 385 (1853).

any further, we may briefly observe the general characteristics of fluorescence.

Fluorescence only appears while the substance is under the influence of the exciting ray ; as soon as the latter is withdrawn the fluorescence ceases. This behaviour distinguishes the phenomenon from phosphorescence, which persists after the stimulating source is removed. Fluorescent substances can be divided into two classes, according to the spectrum of the fluorescent light. On the one hand we have the elements which in the state of vapour give fluorescent spectra consisting of lines,[1] and on the other we find complex substances whose fluorescent spectra are banded. It may be observed that the bands in the latter class of substance usually show a well-defined maximum of intensity. The wave length of the fluorescent light varies within wide limits ; in most of the known fluorescent compounds it occurs in the visible portion of the spectrum ; but recently Stark and Meyer have found[2] that numerous benzene derivatives possess an ultra-violet fluorescence. Fluorescence in the infra-red has not yet been observed.

The relations between the absorption of light and fluorescence are very important. Fluorescence is not excited by light of every wave length; it is produced only when the incident rays contain vibrations which the medium is capable of absorbing. This was first demonstrated by Stokes in the following manner : If a ray of solar light is allowed to pass through two consecutive layers of the same fluorescent medium, it is found that the second layer does not fluoresce. Evidently the first layer deprives the beam of light of all the vibrations which the medium can absorb, consequently the second thickness does not fluoresce. It is clear that the energy which is thrown off during fluorescence is derived from the absorbed vibrations. The relation between absorption and fluorescence is, to a certain extent, reciprocal; not only can absorption cause fluorescence, but fluorescence, in many cases, increases the intensity of absorption. This interesting fact

[1] *Phil. Mag.*, [6] **10**, 52 (1905).
[2] *Phys. Zeit.*, **8**, 250 (1907).

was first demonstrated by Burke,[1] and it has recently been closely studied by Nichols and Merritt,[2] who investigated the relation between the intensity of the incident ray and the absorption caused by the fluorescence. They found that, if the intensity of the incident light is gradually raised, the absorption due to fluorescence increases to a constant value.

We may now turn to the relations between the wave lengths of the absorbed and fluorescent light. It was shown by Stokes[3] that incident light of a given wave length may excite a fluorescence consisting of several different rays; and, conversely, that a given ray in the fluorescent spectrum may correspond to absorbed light of different wave lengths. Stokes further claimed to have established the law that the fluorescent light always has a lower refrangibility, or a greater wave length than the absorbed vibrations which excite it. This relation, known as " Stokes' law," has been submitted to searching tests, and in recent years exceptions to it have been found,[4] for example, in chlorophyll, eosine, and fluoresceine.

It is generally agreed that the fluorescent light is due to vibrations within the medium which are set up by the impact of the absorbed light waves; these induced vibrations are communicated to the surrounding ether, and thus reappear as light. Lommel[4] regarded fluorescence as merely due to the resonance of the molecules and component atoms with the absorbed vibrations, and, developing this assumption mathematically, he was able to give a satisfactory explanation of the known relations between the wave length of absorbed and fluorescent light. But this theory has not survived, chiefly on account of the observations of G. C. Schmidt,[5] who discovered exceptional cases which the theory of resonance could not

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[1] *Proc. Roy. Soc.*, **61**, 485 (1897); **76**, 165 (1905).

[2] *Physical Review*, **18**, 447 (1904); **19**, 396 (1905); see also Wick, *Physical Review*, **24**, 407 (1907).

[3] See also Hagenbach, *Pogg. Ann.*, **146**, 377, 505 (1872).

[4] Lommel, *Pogg. Ann.*, **143**, 26 (1871); **159**, 514 (1876); *Wied. Ann.*, **3**, 113, 251 (1878); **8**, 244 (1878); **24**, 288 (1885); see also H. Könen, *Handbuch der Spektroscopie*, Kayser, vol. iv. 1042 (1908).

[5] *Wied. Ann.*, **58**, 517 (1896).

explain. Wiedemann[1] then advanced the theory that the molecule of a fluorescent substance exists in two forms, one of which is more stable than the other. The stable form, on absorbing the energy of the light vibrations, is transformed to the less stable variety, which then spontaneously passes back to the stable form, emitting the previously absorbed energy as the fluorescent light. The two varieties of the substance may be produced by the shifting of an atom within the molecule, and Wiedemann considers that the fluorescent light is directly due to the vibrations in the ether which are set up by the motion of this atom. In this theory, the older idea of resonance is abandoned; it is no longer supposed that the fluorescent vibrations are directly excited by the absorbed waves, but it is instead assumed that they are set free by the action of light on the molecule.

Wiedemann's theory needs but slight alteration[2] to bring it into line with more modern views. Drude[3] has shown that the vibrations of the atom itself, or the group of positive electrons, must correspond to the infra-red portion of the spectrum, whilst those in the visible and ultra-violet are due to the dispersional, or " valency " electrons. If, then, the fluorescent light is due to atomic vibrations, we must expect it always to occur in the infra-red or at least in the neighbouring portion of the spectrum. However, most substances give a blue or violet fluorescence, and it is remarkable that infra-red fluorescence has not yet been detected. We must therefore ascribe the fluorescent vibrations to the valency electrons, and accordingly we see that the second form of the substance required by Wiedemann's theory need not be produced by the movement of an atom, but merely by the change in position of an electron or valency. This modification of the theory is in better accord with chemical facts than the original; thus many fluorescent substances, for example simple derivatives of benzene, have no mobile atoms in their molecule, but nevertheless are capable of changing their

[1] *Wied. Ann.*, **37**, 177 (1889); **54**, 604 (1895); **56**, 201 (1895).

[2] See Voigt, *Arch. Néerl. Sci. Soc.*, [2] **6**, 352 (1901); Nichols and Merritt, *Physical Review*, **19**, 411 (1905).

[3] Drude, *Ann.*, **14**, 677, 936 (1904).

structure by a movement of the valencies. At the same time
it may be observed that the electronic theory of fluorescence
recognizes the possibility of fluorescence in substances contain-
ing a mobile atom, for the shifting of this atom implies a
change in the position of the electrons.

These views of the mechanism of fluorescence have been
developed by physicists independently of chemical evidence ;
and it will therefore be interesting to attempt to deduce from
them the outlines of the connection between chemical constitu-
tion and fluorescence before proceeding to the evidence
collected by chemists. We must expect to find that the
majority of fluorescent substances either contain a mobile
atom or are capable of undergoing a change in structure
simply by a movement of the valencies of the component
atoms. Moreover, any influence which tends to restrain the
movement of this atom or the valency electrons will alter the
wave length of the fluorescent light and lessen its intensity,
or perhaps extinguish it ; conversely, an influence which
favours the intra-molecular change will increase the intensity
of fluorescence. We thus have some indication of the varying
effect of placing substituents in a fluorescent molecule.
Finally, it may be remarked that since unsaturated substances
are especially prone to intra-molecular change, we must expect
to find that many fluorescent substances possess marked
chemical reactivity.

§ 2. *THE INFLUENCE OF SOLVENTS ON FLUORESCENCE*

· In approaching the relations between fluoresence and
chemical constitution, it should be observed that the data
collected by chemists refer to solutions of the compounds in
various media.   We may therefore briefly consider the influence
of solvents on fluorescence.   The effect of the solvent is often
very marked.   A compound may give a strong fluorescence in
some media, and little or none at all in others, and at the same
time the colour of the fluorescence may vary from solvent to
solvent.   The fluorescence of a dissolved substance may be
influenced by—

1. Chemical combination with the solvent.
2. Ionization.
3. Physical properties of the solvent.

We shall consider these separately.

1. *Chemical combination with the solvent.*—The chief examples of this are found with strongly acid or alkaline solvents which combine with basic or acidic compounds, forming salts. The fluorescence of the substance may be heightened or extinguished. Thus diphenyl-pyrone is non-fluorescent in alcoholic solution, but when dissolved in concentrated sulphuric acid it shows a bright fluorescence. On the other hand, S-phenyl di-*p*-nitro phenazothionium hydroxide in alcohol gives a red fluorescence which is removed by the addition of acid.[1] The only theory which satisfactorily accounts for these relations is that advanced by Hewitt, who claims that fluorescence is provoked by double symmetric tautomerism. It may be shown that only the salts of diphenyl pyrone are capable of this tautomerism, whilst with the phenazothionium derivative salt-formation must exclude it. But this explanation cannot be universally applied, *e.g.* to the fact that 2-methyl-3-amino-4-oxy-quinoline is fluorescent[2] only in dilute alkaline or acid solution.
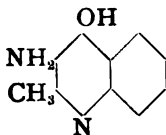
2-Methyl-3-amino-4-oxyquinoline.
Not fluorescent in alcohol.

Here the fluorescence is evidently caused by the formation of ions. We may therefore proceed to consider the effect of—

2. *Ionization.*—The researches of Buckingham[3] and of Knoblauch[4] have shown that ions can be fluorescent, and that

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[1] See p. 457.
[2] O. Stark, *Ber.*, **40**, 3434 (1907).
[3] *Zeit. Phys. Chem.*, **14**, 129 (1894).
[4] *Wied. Ann.*, **54**, 193 (1895).

in most cases the fluorescence of the ions is brighter than that
of the undissociated molecule. Buckingham showed that the
fluorescence of a $\frac{1}{500}$ N. aqueous solution of eosine is weakened
by (*a*) the addition of acids, and (*b*) mixing with very strong
bases ; whilst it is strengthened by increasing the eosine ions
on (*a*) dilution, and (*b*) addition of weak bases. Acid
quinine sulphate gave similar results ; the following table
shows the effect of adding ammonia to a solution of this sub-
stance ; increasing quantities of ammonia diminish the number
of quinine ions present—

TABLE I.

Quinine sulphate concentration.	Ammonia concentration.	Fluorescence.
0·0014	Zero	Strong
0·0014	0·00073	Weak
0·0014	0·0011	Scarcely visible
0·0014	0·0019	None

These facts furnish a simple explanation of the effect of
solvents on fluorescent compounds which form salts ; the fluor-
escence of an electrolyte in strongly ionizing media will be
stronger than in weakly ionizing solvents. It frequently
happens that continued dilution of an aqueous solution at
first increases the fluorescence and then weakens it ; here the
influence of ionization reaches a maximum, and is finally
overcome by the weakening effect of decreasing concentration.
O. Stark[1] has shown that 2-methyl-3-aminoquinoline, like the
previously mentioned hydroxy compound, is inactive, whilst
the ions are strongly fluorescent. He therefore proposes to
employ this substance as an indicator for titrating acids.
The fluorescence persists as long as excess of acid is present,
but it vanishes when the solution is neutralized with alkali.
The interesting experiments of Nichols and Merritt[2] have

[1] *Ber.*, 40, 3434 (1907).
[2] *Phys. Review*, 19, 415 (1904) ; see, however, Carmichel, *Journ. de
Phys.*, [4] 4, 873 (1905).

shown that the conductivity of a solution of eosine or other dyes increases during fluorescence; but it seems uncertain whether this is due to increase of the ordinary dissociation or not.

3. *Physical Properties of the Solvent.*—(a) Selective absorption of light by the solvent may influence the fluorescence in two ways. If the solvent absorbs the vibrations which are required to excite the substance, the fluorescence will be weakened, or perhaps destroyed; and again, if the fluorescent vibrations of the substance correspond with those absorbed by the solvent, the fluorescence will be correspondingly altered. It frequently happens that the emitted ray is of the same colour as the solution, and in these cases the fluorescence is difficult to detect unless the solution be diluted.

(b) *Other physical properties.*—Kundt[1] laid down the rule that the absorption bands of a dissolved substance are pushed further towards the red end of the spectrum the greater the refractive index of the solvent. Stenger[2] claimed to have established a corresponding law for fluorescence; but the more extensive researches of Knoblauch[3] proved that there are many exceptions to it. A connection between the colour of fluorescence of the solute and dielectric constant of the solvent has recently been observed by Kauffmann and Beisswenger;[4] but no relation of a general character can be expressed. In the case of dimethylnaphtho-eurhodine the fluorescence moves towards the red end of the spectrum with increase of the dielectric constant of the solvent.

It is scarcely necessary to remark that in all these experiments dealing with the effect of solvents there have been only a few quantitative measurements of the fluorescence; hence, perhaps, the indefinite nature of the results.

We shall now examine in detail the relations between fluorescence and the chemical constitution of carbon compounds.

[1] *Wied. Ann.*, **4**, 34 (1878).
[2] *Wied. Ann.*, **38**, 201 (1886).
[3] *Wied. Ann.*, **54**, 193 (1895).
[4] *Zeit. Phys. Chem.*, **50**, 350 (1904).

§ 3. *EARLIER RESEARCHES ON FLUORESCENCE AND CONSTITUTION*

The earliest known fluorescent compounds were obtained from plants, but the constitutions of these substances are very intricate, and are imperfectly known even at the present time. The majority of fluorescent compounds of known structure have been produced by synthetical methods, and it is only within recent years that the accumulated data have become sufficient to enable the influence of constitution to be studied with some prospect of success. The first attempt in this direction was made by Liebermann,[1] who studied the fluorescence of anthracene derivatives. It was found that fluorescence is shown only by the compounds which contain the group—

$$\begin{array}{c} \text{M} \\ | \\ -\text{C}- \\ | \\ -\text{C}- \\ | \\ \text{M} \end{array}$$
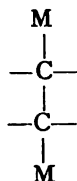
M = monovalent group

placed between two benzene nuclei; when this is converted to the similarly situated quinone group
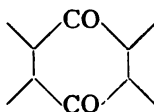
the fluorescence disappears.

The results obtained by Spring [2] a few years later seem to show that fluorescence is characteristic of the benzene nucleus, since hydrocarbons containing this structure are always,

---

[1] *Ber.*, **13**, 913 (1880).
[2] *Bull. Soc. Roy. de Belgique*, 165 (1897).

though perhaps faintly, fluorescent, whilst fatty and alicyclic hydrocarbons never fluoresce.

These researches clearly contain the idea that fluorescence is conditioned by the presence of particular atomic groupings; but neither Liebermann nor Spring extended his researches beyond these special groups of compounds.

§ 4. *FLUOROPHORES*

R. Meyer, however, in 1897, undertook[1] a systematic survey of fluorescent compounds, and he was able to detect a number of groups whose presence tends to excite the molecule to fluorescence. He called these groups " fluorophores," in analogy to the term " chromophore," which had been previously applied by Witt[2] to colour-exciting groups. A list of the fluorophores is given below; it will be seen that they are composed of six-membered heterocyclic systems.
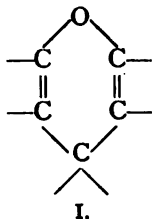
Occurring in derivatives of pyrone, xanthone, and fluorescein.

I.
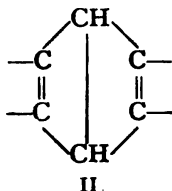
Occurring in the anthracene group.

II.

[1] *Zeit. Phys. Chem.*, **24**, 268 (1897); *Ber.*, **31**, 510 (1898); **36**, 2967 (1903).

[2] *Ber.*, **9**, 522 (1876).
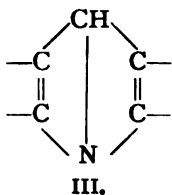
In the acridine group.

III.
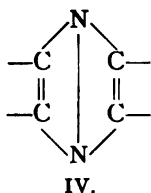
The azine arrangement, occurring in safra-nines.

IV.
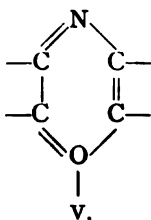
The oxazine group, found in resorufine, etc.

V.
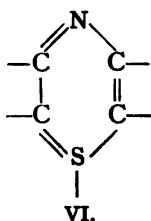
Thiazine group, in methylene blue, etc.

VI.

Many other groups might be added to this list, but those quoted are the more important examples. We may illustrate the method by which Meyer detected these fluorophores with the example of the pyrone arrangement. Both fluorescein (I.) and fluorane (II.).
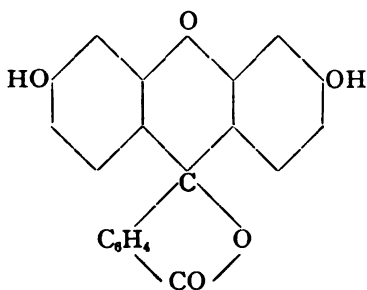
Fluorescein.
(Green fluorescence in alkali.)
I.
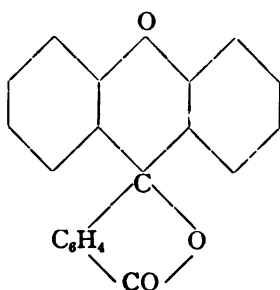
Fluorane.
(Green fluorescence in H_2SO_4.)
II.

are strongly fluorescent, but phenolphthalein (III.)—a sub-
stance which does not contain the bridge-oxygen—
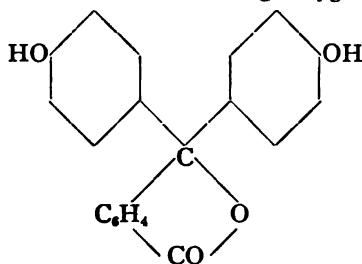
Phenolphthalein.
(Not fluorescent.)
III.

does not fluoresce. Further, neither *o.* cresolphthalein nor *a*
naphthophthalein are fluorescent
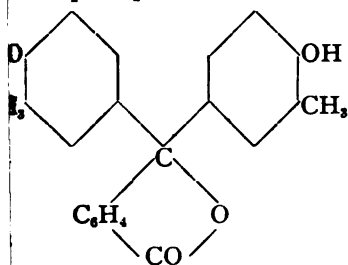
o. Cresolphthalein.
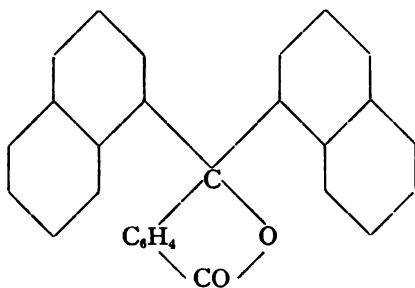
a Naphthophthalein.

(Not fluorescent.)

whilst the corresponding fluoranes, which contain the oxene ring, exhibit a brilliant fluorescence.
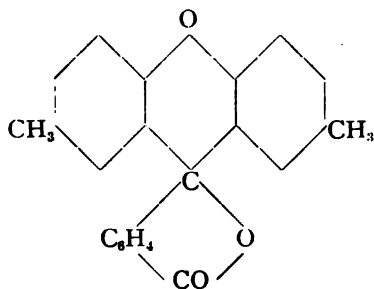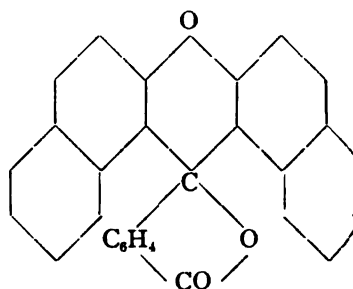
p. Cresofluorane.   *a* Naphthofluorane.

From these and similar facts it appears that the fluorescence is conditioned by the presence of the oxene ring. The other fluorophores mentioned can be determined in a similar manner. It must not be supposed that the mere presence of a fluorophore in a molecule is always sufficient to call forth fluorescence, since in most cases the group must be situated between dense atomic complexes such as benzene nuclei. The following substances serve to illustrate the relation.
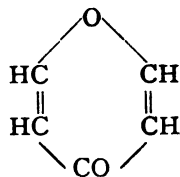
γ Pyrone.
(Not fluorescent.)
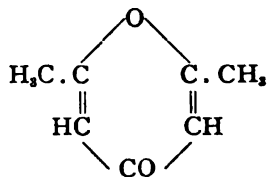
Dimethyl-pyrone.
(Not fluorescent.)
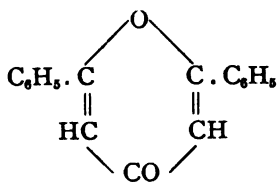
Diphenyl-pyrone.
(Fluorescent in conc. H_2SO_4.)
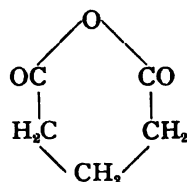
Glutaric anhydride.
(Not fluorescent.)
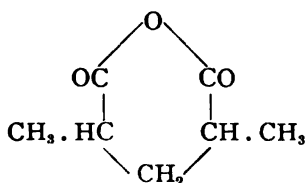
Dimethyl glutaric anhydride.
(Not fluorescent.)
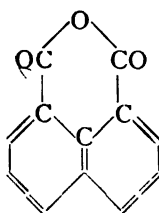
Naphthalic anhydride.
(Fluorescent.)
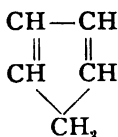
Cyclopentadiene.
(Not fluorescent.)
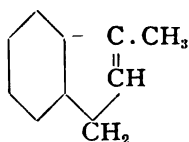
1-Methyl indene.
(Weak fluorescence in
H_2SO_4.)
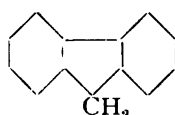
Fluorene.
(Bright fluorescence.)

Substitution.—We thus see that the effect of attaching benzene nuclei to the simplest derivative of the fluorophore tends to excite the latent fluorescence ; but simple groups such as methyl or ethyl are not sufficient. The interesting observations of Henrich and Opfermann [1] in the oxazole series show that the stimulating effect of the benzene nucleus is not merely due to the mass of this complex, but to some other property possessed by the peculiar arrangement of its atoms.
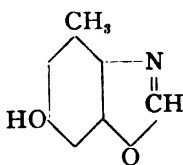
Oxy-tolu-oxazole.
(Not fluorescent.)
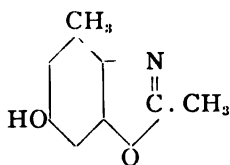
μ Methyl oxy-tolu-oxazole.
(Not fluorescent.)

[1] *Ber.*, **37**, 3108 (1904).
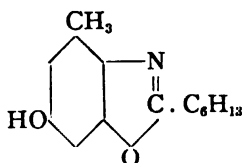
μ Hexyl oxy-tolu-oxazole.
(Not fluorescent.)
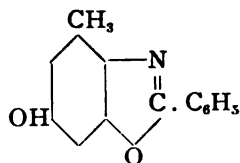
μ Phenyl oxy-tolu-oxazole.
(Fluorescent in H_2SO_4.)

The introduction of simple inorganic groups to a fluorescent molecule depresses the fluorescence, and, according to Meyer, the decrement is roughly controlled by the number and mass of the substituents, being less when they are few and light, and greater when they are numerous and heavy. Thus we have the fluoranes :
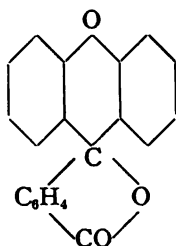
Fluorane.
(Strong fluorescence.)
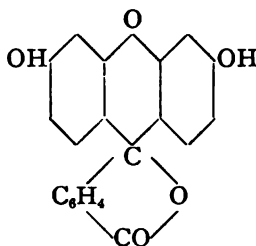
Dioxyfluorane.
(Medium strength)
OH = 17.
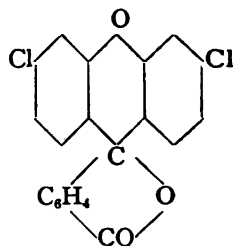
Dichlorofluorane
(No fluorescence)
Cl = 35·5.

and the derivatives of fluorescein (see Table II., p. 439).

In the latter portion of the table we see that the fluorescence diminishes in passing through the series of the tri-tetra-hexachloro derivatives, and also on passing from the mono-bromo to the mono-iodo fluorescein. But it is also evident that, besides the mass and number, the chemical nature of the groups influences the fluorescence ; for the nitro group, although of smaller mass than bromine or iodine, causes a greater depression than either. All observers agree that the nitro group is particularly adverse to fluorescence. Meyer

TABLE II.

Substance.	Fluorescence.	Mass of substituents.
Fluorescein	Medium . .	—
Dibrom-fluorescein	Weak . . .	160
Tetrabrom-fluorescein	Weak . . .	320
Tetraiodo-fluorescein	None . . .	508
Dibrom–dinitro-fluorescein	Very weak .	206
Tetranitro-fluorescein	None . . .	184
Fluorescein from [1]—		
Naphthalic anhydride	Very intense .	o
Mono-bromo-naphthalic anhydride .	Very intense .	80
Tri-chloro-naphthalic anhydride . .	Intense . .	106·5
Iodo-naphthalic anhydride . . .	Intense . .	127
Tetra-chloro-naphthalic anhydride .	Less intense .	142
Hexa-chloro-naphthalic anhydride	Slight . . .	213
Tri-iodo-naphthalic anhydride . .	Faint . . .	381
Di-nitro-naphthalic anhydride. . .	Very faint. .	92

arranges the more commonly occurring groups in the following order of depressing action—

Group . . . $NO_2 > I > Br > Cl > OH$

Mass . . . 46   127   80   35   17

Closer examination of the data shows that the action of substitutents varies according to their position in the molecule; in some positions an otherwise harmless group may destroy the fluorescence of the parent substance. This may be illustrated by comparing fluorescein with hydroquinone phthalein—
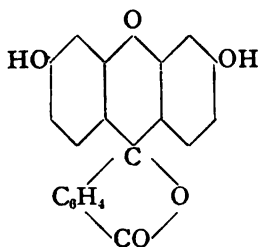
Fluorescein.
(Medium strength.)
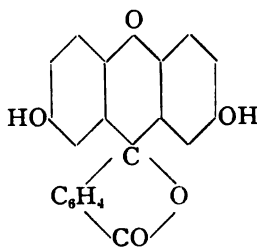
Hydroquinone phthalein.
(No fluorescence.)

[1] Francesconi and Bargellini, *Gazz. Chim. Ital.*, **32.**, II., 73 (1902).

or the three orcine-phthaleins with one another.

(Weak fluorescence.)

(No fluorescence.)

(No fluorescence.)
Orcine-phthaleins.
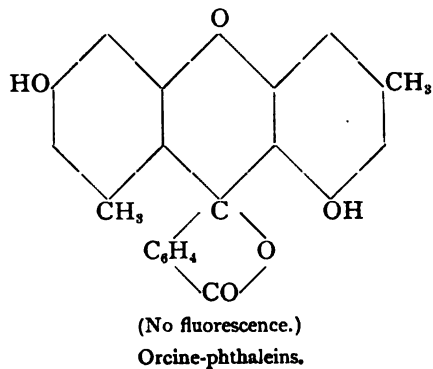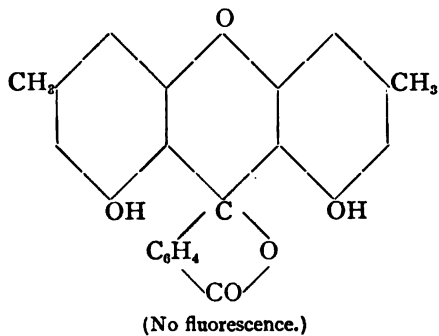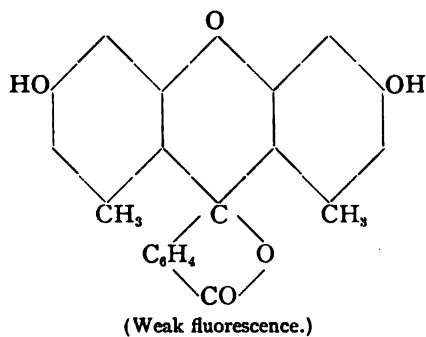
The theory of fluorophores, in its original form, affords no explanation of the relation between chemical structure and fluorescence; but it forms an excellent means of classifying fluorescent compounds, and has thus served as a preliminary step in the solution of the problem. On account of the researches made by Stark [1] on ultra-violet fluorescence, Meyer [2] has recently inverted his former view that the fluorophore is the seat of fluorescence, and that this is merely called forth by the addition of benzene nuclei. Stark and Meyer [2] find that benzene, naphthalene, anthracene, phenanthrene, benzophenone, hydroquinone, resorcinol, and catechol and many other aromatic compounds exhibit ultra-violet fluorescence. They therefore conclude that in aromatic substances the benzene nucleus is the carrier of fluorescence; whilst the fluorophores and various substituents act so as to bring the fluorescent vibrations within the visible portion of the spectrum. The condensation of benzenoid nuclei acts in the same manner. This explanation of the part played by the benzene nucleus is undoubtedly correct, and it is significant that Kauffmann from another standpoint has obtained a similar result. [3]

§ 5. *THE THEORY OF KAUFFMANN—LUMINOPHORES AND FLUOROGENS*

The vapours of many substances become luminous when exposed to the action of a Tesla discharge, but the appearance of luminescence depends on the pressure under which the vapour is placed. Low pressures are favourable; in fact, many substances which do not respond to the discharge at atmospheric pressure become luminous under diminished pressure. Hemptinne [4] made experiments to find a relation between the molecular weight of a substance and the pressure at which its vapour becomes luminous; but he could not detect any definite

[1] *Physikal. Zeit.*, **8**, 81, 248 (1907); **9**, 85 (1908).
[2] *Physikal Zeit.*, **8**, 250 (1907).
[3] See also H. von Liebig, *Ann.*, **360**, 128 (1908).
[4] *Zeit. Phys. Chem.*, **22**, 358; **23**, 483 (1897).

relation, and concluded that luminescence is chiefly determined by constitution.

The relations between constitution and luminescence have since been very fully investigated by Kauffmann.[1] Luminescence is shown by substances of different types; but it is more pronounced with cyclic compounds, and especially so with derivatives of benzene. A comparison of luminescent compounds shows that these possess in common certain groups which evidently provoke the luminescence. Kauffmann has called these groups " luminophores." It is clear that in aromatic substances, *e.g.*—

$$C_2H_5$$

$$C_2H_5 \diagup \diagdown C_2H_5$$
$$C_2H_5 \diagdown \diagup C_2H_5$$

$$C_2H_5$$
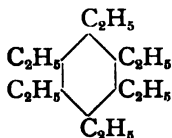
Hexa-ethyl-benzene.

$$NH_2$$
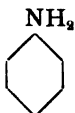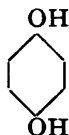
Aniline.
(Violet-blue luminescence.)

$$OH$$

$$OH$$

Hydroquinone.

the seat of luminescence is in the benzene nucleus; but it should be noted that this does not become a true luminophore until auxochromes[2] are introduced, benzene itself being non-luminescent under normal conditions. Thus dimethylaniline, aniline, and hydroquinone are luminophores, whilst the dimethylamino, amino, and hydroxyl groups are the auxochromes.

Kauffmann points out that the property of luminescence thus assumed by the benzene ring is generally accompanied by

1. Increased reactivity ;
2. A tendency to yield *p*. quinones on oxidation ;
3. Optical[3] and magneto-optical anomaly.[4]

[1] *Fluorescenz und chemischer Konstitution*, Stuttgart, 1906 ; *Die Auxochrome*, Stuttgart, 1907 ; *Ber.*, **33**, 1725 (1900) ; **34**, 682 (1901) ; **35**, 473, 1321, 3668 (1902) ; **36**, 561 (1903) ; **37**, 2613 (1904) ; **38**, 789 (1905) ; **39**, 2722 (1906) ; **40**, 843, 2338, 2341 (1907); *Zeit. Phys. Chem.*, **55**, 547 1906) ; *Ann.*, **444**, 30 (1906).
[2] Colour and Constitution, p. 348.
[3] Refractive Index, p. 284.
[4] Magnetic Rotation, p. 484.

Moreover, it is found that these properties are at a maximum when the luminescence is strongest, and any influence which modifies them tends to extinguish the luminescence. It is thus clear that in a luminescent aromatic compound the benzene complex is in an abnormal state.

The magneto-optical anomaly may be conveniently employed as a rough quantitative measure of the divergence from the normal. If the condition of the ring-system in benzene is chosen as the normal, the normal magnetic rotation of a substance may be calculated from the rotation of benzene, making allowance for the groups inserted. Thus, using the data collected by Perkin,[1] we find that the normal value for aniline is 12·25—

$$\text{Aniline } C_6H_5NH_2$$
$$C_6H_6 = 11\cdot284$$
$$N = 0\cdot717$$
$$H = 0\cdot254$$

Mol. rotation (calc.) $= 12\cdot25$
Mol. rotation (obs.) $= 16\cdot07$

Anomaly $= + \ 3\cdot82$

The difference between this and the observed rotation represents the magneto-optical anomaly. It may be observed that this is not the absolute anomaly, which would be obtained by taking the sum of the rotatory effects of the elements as the normal, but it expresses the anomaly relatively to benzene. In the following list the magneto-optical anomaly (A) and the luminescence of various compounds are represented. It will be seen that the addition of groups like amino and hydroxyl (auxochromes) to the benzene system raises the luminosity, and at the same time produces the anomaly.

Moreover, the anomaly and luminescence run parallel, the brighter the luminosity the greater is the anomaly of the substance. Some substituents, like the nitro and carbo-ethoxyl groups, cause a negative anomaly, and here the benzene

[1] Magnetic Rotation, p. 483.

TABLE III.

Substance.	A.	Luminescence.
Nitrobenzene	− 2·15	None
Ethyl benzoate	− 0·38	None
Bromobenzene	− 0·09	None
Benzene	± 0·0	Very weak at ordinary pressures
Phenetole	+ 1·61	Very weak
Hydroquinone dimethyl ether .	+ 3·0	Strong
Aniline	+ 3·82	Strong
Dimethyl aniline	+ 8·59	Intense
Dimethyl *p.* phenylene diamine .	+10·97	Very intense

nucleus recedes from the condition necessary to luminescence. The more important structural changes which induce luminescence in the benzene system are collected in the annexed table; and they are arranged roughly in order of descending activity.

TABLE IV.

Examples.

1. Substitution of dialkylamino group . . . Dimethylaniline A=8·59
2. Substitution of amino group . . . . . Aniline . . . A=3·82
3. Fusion of benzene nuclei . . . . . . Naphthalene . A=4·60
4. Substitution of ethoxyl group . . . . Phenetole . . A=1·61
5. Substitution of acetamino group . . . . Acetanilide . . A=1·95

Similar relations may be detected between luminosity and optical anomaly; but here they are less distinct, since the refractive anomaly is much smaller.

It has been observed that the more pronouncedly luminous compounds are readily oxidized to derivatives of *p.* quinone, and from this and other facts, which need not be here mentioned, Kauffmann concludes that the benzene nucleus in these substances must approach the *p.* quinonoid state. The limiting or ideal condition for luminescence would be that represented by Dewar's formula—

in which a para bond is assumed; this is accordingly termed the "D condition." It must not be thought that this formula is intended to show the actual structure of the luminous system. Indeed, with any static formula it is impossible adequately to do this, since the formula merely represents an ideal condition which the nucleus approaches more or less closely during the oscillation of its valencies. Whether this view of the state of the nucleus is correct or not, it is clear that we are here dealing with a condition similar to that which has been already referred to in the study of optical anomaly and the effect of conjugation. We there adopted as an explanation of the anomaly, that the abnormal state is due to the disturbance of the closed system of affinities in benzene caused by introducing a group of strong residual affinity. If the substituting group becomes saturated the anomaly falls and the luminescence weakens. For example—

TABLE V.

Substance.	A.	Luminescence.
Aniline	3·82	Strong
Acetanilide	1·95	Weak
Aniline hydrochloride . .	0·14	(?)
Dimethyl aniline . . .	8·59	Intense
Dimethyl aniline hydro-chloride	0·02	(?)
Phenol	0·66	Scarcely visible
Phenyl acetate	−0·33	None

Finally, it should be noticed that when two of these groups are present in *para* positions they reinforce one another; but, if in *meta* or *ortho* situations, their action seems to be opposed. Thus we have—

Substance.	A.	Luminescence.
Resorcinol	0·61	None
Catechol.	1·35	Scarcely visible
Hydroquinone dimethyl ether	3·00	Bright

Fluorogens.—We may now turn to the relations between luminescence and fluorescence. The addition of an auxochrome to the benzene ring is not alone sufficient to cause fluorescence; but another group, called the fluorogen, must be added. Thus in dimethylaniline we have as auxochrome the dimethylamino group, and the substance consequently exhibits a strong luminescence; but fluorescence is latent, and is not provoked until a fluorogen is inserted. If carboxyl is introduced we have the fluorescent dimethylanthranilic acid, and here the carboxyl group is the fluorogen. We see, then, that a luminophore becomes fluorescent by the addition of a fluorogen. The following is a list of fluorogens with a few examples illustrating their occurrence :—

(Fl = fluorogen ; A = auxochrome ; Lum = luminophore.)

The carboxyl group, —COOH
Examples—
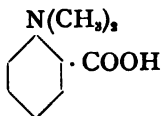
A = N(CH₃)₂.
Fl = COOH.

Dimethyl anthranilic acid.
(Violet fluorescence.)
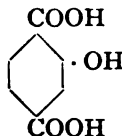
A = OH.
Fl = COOH.

Oxyterephthalic acid.
(Violet fluorescence.)

The acrylic acid group, —CH=CH—COOH
Examples—
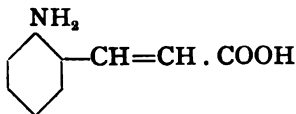
A = NH₂.
Fl = CH=CH . COOH.

o. Aminocinnamic acid.
(Green-blue fluorescence.)
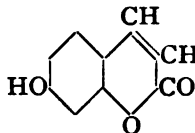
A = OH and O—
Fl = CH=CH—CO--

Umbelliferone.
(Blue fluorescence.)

The ethylene linkage, —CH=CH—

Examples—

OCH₃ structure:

$$CH_3O - \underset{OCH_3}{\overset{OCH_3}{C_6H_3}} - CH{=}CH{-}CH_3$$
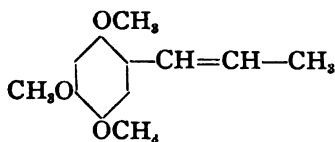
A = OCH₃
Fl = —CH=CH—

Asarone.
(Blue fluorescence.)

α Methyl indole structure

A = NH—
Fl = —CH=CCH₃—
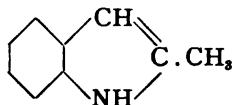
α Methyl indole.
(Green fluorescence.)

Conjugated ethylene linkages, —CH=CH—CH=CH—

Examples—

CH₃O—C₆H₄—CH=CH
                    |
CH₃O—C₆H₄—CH=CH
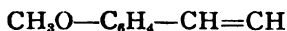
A = OCH₃
Fl = —CH=CH
        |
     —CH=CH

Di-methoxyphenyl-butadiene.
(Violet fluorescence.)

NH₂

Lum

A = NH₂

Fl =
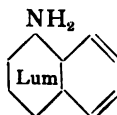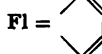
α Naphthylamine.
(Violet fluorescence.)

The benzene ring,

Examples—

NH₂ Lum

NH

A = NH— and NH₂

Fl =
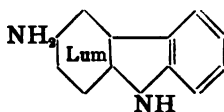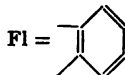
3 Aminocarbazole.
(Blue fluorescence.)

The carbonyl group, —CO—
Examples—
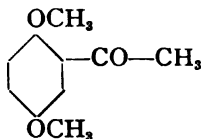
OCH₃

—CO—CH₃

OCH₃

A = —OCH₃
Fl = —CO —CH₃

2-5-Dimethoxyacetophenone.
(Blue fluorescence.)

O

HO

CO
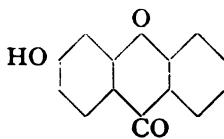
A = OH and
Fl =

3 Oxyxanthone.
(Blue fluorescence.)

The azo-methine group, —CH=N— and the para and ortho quinonoid rings are further examples of fluorogens.

Fluorescence is further determined by the relative positions of the fluorogen and the auxochromes. If there are two auxochromes and one fluorogen present, fluorescence occurs only if their positions are unsymmetrical. Thus only substances of the following structure will be fluorescent.

A

Fl

A

A

A

Fl

Fl

A

A
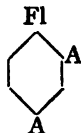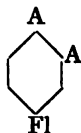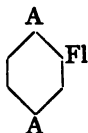
If three auxochromes and one fluorogen are present, fluorescence does not occur when the fluorogen and two of the auxochromes are adjacent, so that fluorescence is to be expected only with the constitutions—

A

Fl

A

A

A

A

A

Fl
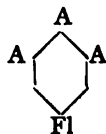
When the fluorogen and an auxochrome are in *ortho* positions, they may form part of a cyclic system, as with the 3-oxyxanthone shown in the list at the head of the page.

The action of a fluorogen further depends on the residual affinity of the group. Adopting Thiele's theory of partial valency, we may say that a fluorogen has greater influence when it has more residual affinity available to unite with that of the luminophore. Thus in dimethoxy-acetophenone (I.) —
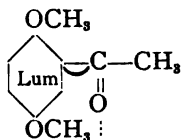
I.*
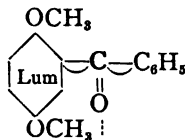
II.*

the whole of the unsatisfied valency of the carbonyl group is at the disposal of the luminophore; the fluorescence is therefore stronger than with dimethoxy-benzophenone (II.), where the partial valency of the carbonyl is shared by the luminophore and the phenyl group. Further illustration may be taken from tetramethoxy-stilbene (I.) and tetramethoxy-diphenyl propylene (II.).
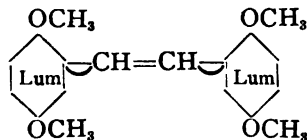
I.

Strong green fluorescence.
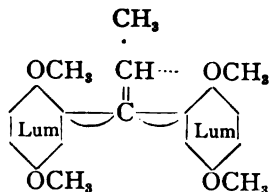
II.

Very weak blue fluorescence.

In the former substance, which is strongly fluorescent, the entire unsaturated affinity of an ethylenic carbon atom is available for each luminophore; whilst in the weakly fluorescent propylene derivative, the partial valency of one unsaturated carbon atom is distributed between two luminophores.

Kauffmann has further studied the effect on fluorescence

* In the formulæ the curved lines which represent the partial valencies are shown in different thickness to illustrate the relative strengths of the action.

of simple substituents, and the results were similar to those obtained by Meyer.

Reviewing the results of this work, we see that in aromatic compounds the benzene nucleus is the seat of fluorescence, but this is not evoked until two kinds of groups—the auxochrome and fluorogen—have been introduced in certain positions. The insertion of an auxochrome excites luminescence, indicating the approaching state of fluorescence, and the addition of a fluorogen to the luminophore completes the process. The activity of an auxochrome seems to depend on the strength of its residual affinity, or the disturbance which it produces in the balance of the affinities of the nucleus. Also the stimulating action of a fluorogen depends on the strength of the residual affinity which it places at the disposal of the luminophore. It thus seems difficult to draw any fundamental distinction between an auxochrome and a fluorogen, but it may be observed that the former are usually simple groups of well-marked chemical character, whilst fluorogens are of weaker affinity and more complex structure. It would be interesting to compare the activity of fluorogens with the optical anomaly they produce when attached to the luminophore; but this has not been done.

Thus the theory of Kauffmann is a step in advance of that of Meyer, since it offers a more complete explanation of the action of substituting groups. Also Francesconi and Bargellini [1] have admitted the important part played in fluorescence by the benzene nucleus; and recognizing that the observations of Meyer and Kauffmann are limited to visible fluorescence, they claim that all aromatic compounds are fluorescent, and that it is premature to attempt to explain the action of substituents. They are content with classifying substituents according to their action on the fluorescence of the parent substance; those which raise the fluorescence are called "auxoflores," and those which depress it, "bathoflores." Thus we have—

Auxoflores

$$—NH_2 —NHR, \text{ etc., } —SO_3H, —CN, —COOH, \text{ and}$$
$$—CH=CH—$$

[1] *Atti. R. Accad. dei Luicei Roma*, [5] **15**, II. 184 (1006)

Bathoflores

$$-N=N-, \text{ Cl, Br, I, NO}_2, \text{ and } -COCH_3$$
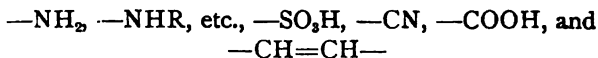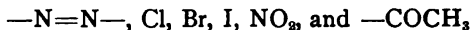
We see, then, that the evidence collected by chemists, proving the origin of fluorescence to be in the benzene nucleus, accords with the physical theory which requires the presence of mobile negative electrons or valencies in the fluorescent molecule. Both chemical[1] and physico-chemical[2] evidence shows that the affinities of the benzene system are in a state of continual oscillation, which causes the molecule to pass through several distinct phases of structure.

§ 6 *THE THEORY OF HEWITT—DOUBLE SYMMETRIC TAUTOMERISM*

Clear evidence of the connection between tautomeric change and fluorescence was first brought forward by Hewitt.[3]

Since the wave length of the fluorescence is different from that of the absorbed light, Hewitt considers that a fluorescent substance must exist in two interchangeable forms; one of these absorbs the energy of the incident light, and passes over to the other form, which, re-emitting the energy of the absorbed light, returns to the original state. Hence, fluorescence would be shown by—

(1) Associated substances, in which there is a continual interchange between the associated and unassociated molecules.

(2) Tautomeric compounds.

Now it is clear that fluorescence will further depend on the ease with which one form is converted to the other. Substances in which more energy is required to accomplish the tautomeric change will show weaker fluorescence, and in extreme cases there will be no fluorescence. It is probably for this reason that we never find fluorescence due to association. Adopting this view, Hewitt has shown that there is a particular kind

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[1] Collie, *Trans. Chem. Soc.*, **71**, 1013 (1897).

[2] Baly and Collie, *Trans. Chem. Soc.*, **87**, 1332 (1905).

[3] *Zeit. Phys. Chem.*, **34**, 1 (1900); *Journ. Soc. Chem. Ind.*, **22**, 127 (1903).

of tautomeric change which must be especially adapted to fluorescence. The nature of this tautomerism will be readily understood by reference to an example. We may take fluorescein. This substance may exist as either the double hydroxyl form II., or the quinonoid form IA., which may be also written as IB.

IA. II.

IB.
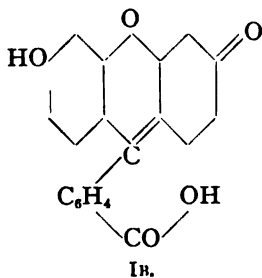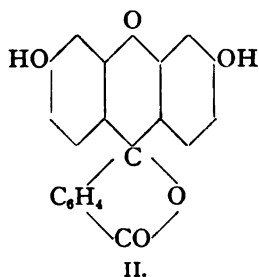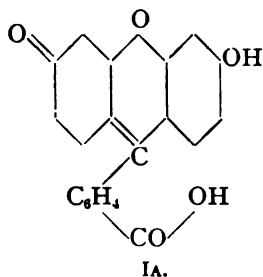
The molecule starting from IA. will pass to II., and thence to IB., when the process is repeated in the reverse direction. It will be seen that IA. and IB. are chemically identical, so that the process does not require the existence of a third tautomeric form. This is called double symmetric tautomerism, since it can occur only in those compounds in which the tautomeric change may involve either of two symmetrically arranged identical groups. The changes in the molecule of the substance are analogous to the movements of a swinging pendulum. The limiting positions in the amplitude of vibration correspond to the forms IA. and IB., and the position of rest through which

the pendulum swings would be represented by the form II. It is clear that the changes involved in this kind of tautomerism would take place rapidly, and would require but little external energy for their maintenance.

If this theory be accepted we must expect to find that all substances showing double symmetric tautomerism are fluorescent, and this is confirmed by experience. The following are some of the chief examples.

Anthracene—
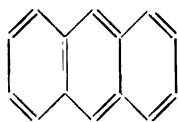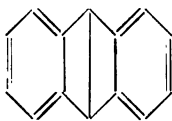
IA.   II.   IB.

Fluorane (in conc. H_2SO_4)—
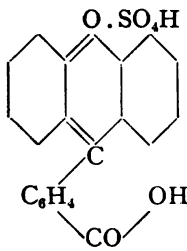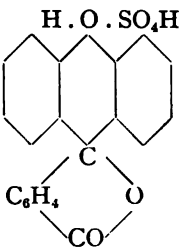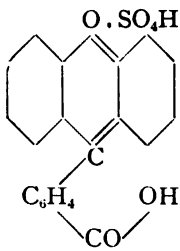
IA.   II.   IB.

Diphenyl pyrone (in conc. H_2SO_4)—
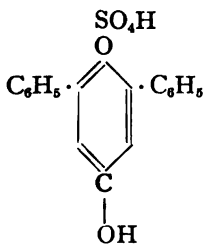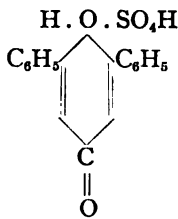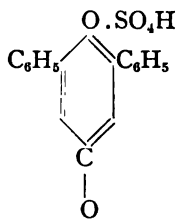
IA.   II.   IB.

Methylene blue—
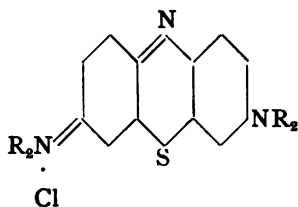
IA.
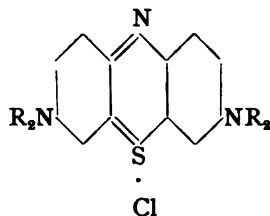
II.
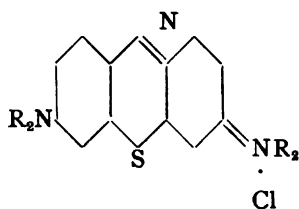
IB.

Pheno-safranines—
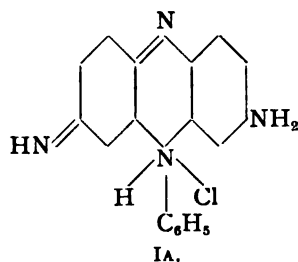
IA.
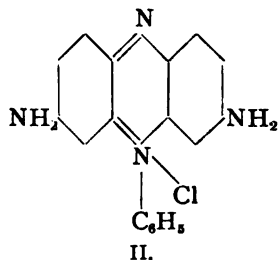
II.
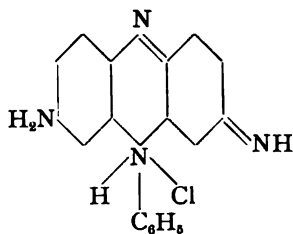
IB.

Diamino acridine—

IA.

II.

IB.
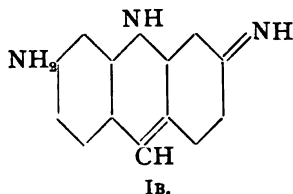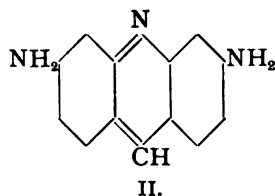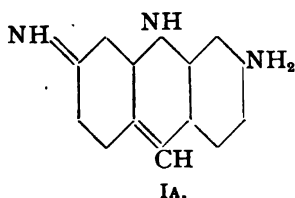
All these substances are strongly fluorescent. The hypothesis also affords an explanation of the fact that whilst many substances of symmetrical structure are fluorescent, the closely allied compounds of unsymmetrical structure are usually non-fluorescent. Thus aposafranine
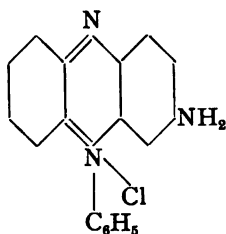
Aposafranine.
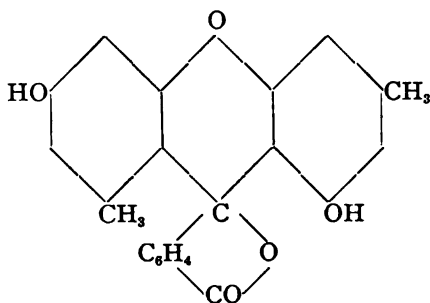
Orcinephthaleine.

and the orcinephthaleine mentioned are not fluorescent; and the symmetrical nitro compound (I.) is strongly fluorescent in contrast to the inactive unsymmetrical isomeride (II.).
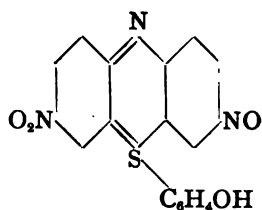
p. Di-nitro *S*. oxyphenyl phen-
azothionium hydrate.
I.
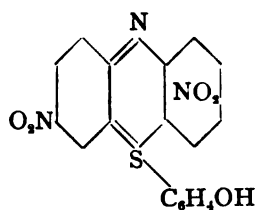
Iso-di-nitro *S*. oxyphenyl phen-
azothionium hydrate.
II.

It will be readily seen from the formulæ of these sub-
stances that the unsymmetrical compounds cannot exhibit the
double symmetric tautomerism. The theory also explains the
exceptional behaviour of certain nitro-compounds. The nitro
group usually depresses or removes fluorescence, but the di-
nitro derivative of *S*. phenyl phenazothionium (A) shows a
bright green fluorescence in contrast to the weak red of the
diamino compound (B).

(A)[1]

Iᴀ.

II.

Iʙ.

(B)[1]

$$C_6H_4OC_2H_5$$

This exceptional behaviour may be explained by the fact that in the amino compounds double symmetric tautomerism is impossible, whilst in the former substance the nitro groups encourage it by forming the nitronic thetine (IA).

It should be further noticed that this theory is the only one which gives a satisfactory account of the influence of acid solvents on fluorescence. For example, the usual formula of diphenyl pyrone does not admit double symmetric tautomerism; but in presence of strong acids a salt would be formed[2] which, being capable of this tautomerism,[3] will be fluorescent. This agrees with experiment, since diphenyl-pyrone in neutral solvents like alcohol is non-fluorescent, but is brightly fluorescent in strong acids. The fluorescence of fluorane in concentrated sulphuric acid may be explained in the same way, and it may be noticed that Hewitt was here successful in isolating the sulphate.[4] Moreover, the fluorescence of the previously mentioned dinitro *S.* phenyl phenazothionium hydrate is removed by addition of acids, and it is clear that the salts which are then formed cannot exhibit the double symmetric tautomerism, *e.g.*

[1] Smiles and Hilditch, *Trans. Chem. Soc.*, **93**, 145 (1908).
[2] Collie and Tickle, *Trans. Chem. Soc.*, **75**, 710 (1899).
[3] See p. 458.
[4] *Proc. Chem. Soc.*, **18**, 86 (1902).
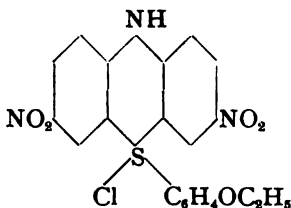
Hewitt seems originally to have claimed that all fluorescent substances show double symmetric tautomerism; but at present this can scarcely be upheld, since many exceptional cases have been found.[1] Nevertheless the importance of the theory must not be overlooked, for it clearly shows that the presence of " labile " valencies favours fluorescence.

In concluding the study of fluorescence it may be observed that hitherto the attention of chemists has been confined merely to visible fluorescence ; ultra-violet and very weak fluorescence in the visible spectum have been neglected. Unless the complete fluorescent spectra are studied as closely as absorption spectra have been, we cannot expect to advance beyond the stage of rough generalizations. Recently, however, Stark[2] and Nichols and Merritt[3] have commenced the systematic study of fluorescence, the former using the photographic and the latter the photometric method ; we may therefore hope for important developments in the near future.

[1] See Francesconi and Bargellini, *Gass. Chim. Ital.*, **32**, II. 73 (1902) ; **33**, II. 129 (1903) ; Silberrad, *Trans. Chem. Soc.*, **89**, 1787 (1906) ; Kauffmann, *Ber.*, **37**, 2941 (1904) ; Meyer, *Phys. Zeit.*, **8**, 254 (1907).

[2] *Phys. Zeit.*, **8**, 81, 248, 250 (1907).

[3] *Phys. Review*, **18**, 414, 447 (1904) ; **19**, 396, 415 (1904).

CHAPTER XIII

MAGNETIC ROTATORY POWER AND CONSTITUTION

§ 1. *INTRODUCTION*

In 1846 Faraday discovered that certain substances when placed in a magnetic field are capable of rotating the plane of transmitted polarized light. He further showed that the magnitude of the rotation directly depends on the length of layer of the substance traversed, and also on the intensity of the magnetic field acting in the direction of the beam of light. These researches are of classical importance, but since they were focussed on the physical nature of the property we need not further discuss them. The first research on the connection between chemical construction and this " magnetic rotation " was published in 1882 by Sir W. H. Perkin, whose efforts, prolonged for more than a quarter of a century, have since yielded almost all that is known of this subject. Thus the relations between constitution and magnetic rotation have been systematically developed by a single observer, with the result that the subject presents a homogeneity rarely found in the relations of other physical properties. The phases through which the development of the relations between this property and constitution has passed are typical of those seen in the history of many other physical properties. In his earlier researches, Perkin succeeded in detecting additive relations, and, having accurately defined these, he then turned to the influence of constitution. Subsequently, by combining the two types of relations, he devised a method of determining constitution which may be said to rank among the more

450

reliable of those furnished by physical properties. Before proceeding to consider these relations between magnetic rotatory power and constitution we shall briefly consider the physical character of the property.

i. PHYSICAL CHARACTER OF MAGNETIC ROTATION

§ 2. *SPECIFIC AND MOLECULAR MAGNETIC ROTATION*

If we imagine a layer of unit length of any substance placed in a magnetic field of unit intensity, and traversed by a beam of homogeneous plane polarized light in the direction of the lines of force of the field, then the rotation which the plane of polarization undergoes at a known temperature is the absolute magnetic rotation of the substance.

To discover the connection between constitution and magnetic rotation it is not necessary to employ absolute values ; all that is required is the value of the rotation expressed in terms of that of some standard body placed under similar conditions. Perkin chose water as the standard on which to base this relative value.

By the relative specific rotation is meant the ratio of the rotations exerted by the substance and the standard in layers of equal thickness at the same temperature and in the same magnetic field. Hence, denoting the specific rotation by r, we have the expression—

$$r = \frac{a}{a} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

Where a is the rotation of the substance, and a that of the standard under identical conditions. If the layers of the substance and standard are of unequal length, say l and λ respectively, then r becomes—

$$r = \frac{a\lambda}{al} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

To compare the rotations of different substances with one another we require to find the rotatory effects of equal

numbers of molecules of the substances in question. A measure of this is given by the molecular magnetic rotation (M), which is expressed as follows :—

$$M = \frac{a\lambda\delta m}{a l d \mu} \qquad \text{. . . . . . (iii)}$$

where m and d are respectively the molecular weight and density of the substance, and μ and δ the corresponding values for the standard. In Perkin's determinations the substance and the standard were examined in tubes of equal length, so that then—

$$M = \frac{a\delta m}{a d \mu} \qquad \text{. . . . . . (iv)}$$

It should be noticed that in equation (iii) the factor m/d is introduced, so that the molecular rotations are strictly comparable only if the different substances are unassociated, or have the same molecular complexity. Now it will be seen, on consulting the chapters dealing with volume relations and surface energy, that there is much evidence to show that the initial members of an homologous series frequently have more complex molecules than the members of high molecular weight; and we thus have a probable explanation of the fact that the molecular rotation of many of the simplest compounds is abnormal.[1] This circumstance will be illustrated later. To obtain the molecular rotation of a dissolved substance we must first calculate the molecular rotation of the solution, and then subtract from this the rotation of the solvent.[2] If the substance is dissolved in the proportion of one molecule to n molecules of solvent, the " average molecular weight " of the solution is equal to $m + nm'$, where m and m' are the molecular weights of the substance and solvent respectively. The molecular rotation (M_s) of the solution may then be expressed as—

$$M_s = \frac{(m + nm')a\lambda\delta}{\mu a l d} \qquad \text{. . . . . (v)}$$

[1] Frankland has discussed the influence of association on optical rotatory power, *Trans. Chem. Soc.*, 347 (1899).

[2] See also Schönrock, *Zeit. Phys. Chem.*, 11, 753 (1893); Wachsmuth, *Wied. Ann.*, 48, 280 (1893).

where a and d are the values experimentally found for the rotation and density of the solution. From this we may obtain the molecular rotation of the solute by subtracting the rotatory effect of the solvent, so that we may write—

$$M = M_s - M'n \quad . \quad . \quad . \quad . \quad \text{(vi)}$$

Where M, M_s and M' are the molecular rotations of the solute, solution and solvent, n being as before the molecular proportion of the solvent. For example, a solution of sulphuric acid which had the composition $H_2SO_4 . 3H_2O$ gave M' = 5·064; hence taking, as usual, the molecular rotation of water as unity, we have M for sulphuric acid in a solution of this strength equal to 5·064 − 3 = 2·064.

If desired, the absolute rotation (R) of a substance can be derived from equation (iv) with the help of the absolute rotation of the standard; if this be ρ then—

$$R = \frac{M\rho d\mu}{\delta m} \quad . \quad . \quad . \quad . \quad \text{(vii)}$$

Probably the most accurate value for the absolute rotation of water is that obtained by Roger and Watson—[1]

$$\rho = 0·01311 - 0·0_64t - 0·0_74t^2$$

where t is a temperature between 4° and 98°.

The magnetic rotation of the plane of polarized light is measured in the same way as the permanent rotation of a substance, but the apparatus is more complex, since an arrangement for placing the substance in a magnetic field is provided. The tube containing the liquid is placed either between the poles or, as in Perkin's latest form of apparatus, in the hollow core of a powerful electro-magnet. The chief precaution to be observed in addition to those of an ordinary polarimetric determination, is in preserving a constant strength of the magnetic field. The rotations of the standard and of the substance are measured in the same tube under identical conditions of temperature and magnetic intensity. For a

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[1] Roger and Watson, *Zeit. Phys. Chem.*, **19**, 357 (1896).

description of the apparatus and details of the method the reader must be referred to the original literature. [1]

The influence of temperature on magnetic rotatory power is not very great, and, as a rule, increase of temperature depresses the rotation. The temperature-effect seems to depend on the constitution of the substance, since Perkin [2] has found that in homologous series it is greater with substances of high molecular weight than the simpler derivatives. The following table shows the magnitude of the temperature-effect for a few aliphatic compounds, and the figure under M represents the fall in molecular rotatory power corresponding to a rise of 100°.

TABLE I.

Substance.	Formula.	M.
Acetic acid	CH_3COOH	−0·049
Propionic acid	C_2H_5COOH	−0·034
Oenanthylic acid	$C_6H_{13}COOH$	−0·113
Propyl bromide	C_3H_7Br	−0·210
Octyl bromide	$C_8H_{17}Br$	−0·288
Ethyl iodide	C_2H_5I	−0·394
Octyl iodide	$C_8H_{17}I$	−0·474
Methylene diiodide	CH_2I_2	−0·863

With aromatic compounds the influence is usually more marked, *e.g.*—

TABLE II.

Substance.	Formula.	M.
Benzene	C_6H_6	−0·477
Toluene	$C_6H_5.CH_3$	−0·530
Benzophenone	$C_6H_5COC_6H_5$	−0·689
Chlorobenzene	C_6H_5Cl	−0·377
Phenyl sulphide	$(C_6H_5)_2S$	−0·996
α Naphthylamine	$C_{10}H_7NH_2$	−1·561

[1] Perkin, *Trans. Chem. Soc.*, 421 (1884); **69**, 1025 (1896); **89**, 608 (1906).

[2] Perkin, *Trans. Chem. Soc.*, **61**, 307 (1892); **69**, 1058 (1896).

ii. MAGNETIC ROTATION AND CHEMICAL CONSTITUTIOI

§ 3. *ISOMERIC COMPOUNDS*

Before proceeding to examine the rotatory effects ·ノ,
individual groups we may obtain some idea of the geneι.ι
nature of the property by considering the rotations of is
merides. In the following list the rotatory powers of son
isomerides are contrasted, and it is seen that the property_
largely influenced by the constitution of the substance. Wit
isomerides of very similar structure the difference in rotatio
is not large; for example, we may refer to the isomeric ester
and hydrocarbons at the beginning of the table; but on th·
other hand, with isomers of widely different chemical natur
the difference in rotation is correspondingly great.

TABLE III.

ISOMERS.

Substance.	M.	Δ	Approximate percentage difference.
Pentane	5·638	0·112	1·9
Isopentane . . .	5·750		
Hexane	6·670	0·099	1·5
Isohexane . . .	6·769		
Propyl formate . .	4·534	0·072	1·6
Ethyl acetate . .	4·462		
Propyl acetate . .	5·487	0·035	0·6
Ethyl propionate . .	5·452		
Ethyl oxalate . .	6·654	0·422	6·3
Methyl succinate . .	6·232		
Ethyl itaconate . .	10·467	0·763	7·3
Ethyl mesaconate . .	11·233		
Nitro isobutane . .	4·99	0·38	7·6
Isobutyl nitrite . .	5·37		
Acetaldehyde . . .	2·385	0·45	22·0
Ethylene oxide . . .	1·935		

The constitutive nature of the property is further demon-
strated by the fact that a given rearrangement of the atoms in
a compound does not always produce the same effect on the
rotatory power. To illustrate this relation we may compare

.al and *iso* compounds. A compound containing a normal
ñ of carbon atoms has always a smaller rotation than an
ñeride in which the chain is branched. The average effect
eplacing the normal by the iso-structure is shown below
for a few classes of compounds, and it is apparent that the
effect, though of the same order, does not remain at a constant
value.

TABLE IV.

Class of compound.	Effect on M of change from *n* to iso structure.	Class of compound.	Effect on M of change from *n* to iso structure.
Hydrocarbons . .	+0·106	Monobasic acids .	+0·132
Iorides . . .	+0·090	Acetic esters . .	+0·117
omides . .	+0·103	Esters of higher	
dides	+0·089	acids . . .	+0·131
Alcohols . . .	+0·160	Aldehydes . .	+0·110

Stereoisomerides.[1]—Similar varying relations are found
etween stereo-isomerides of the ethylenic type, thus—

TABLE V.

Substance.	T.	M.	Δ
Ethyl mesaconate . . .	16°	11·233	0·716
Ethyl citraconate . . .	16	10·517	
Methyl mesaconate . . .	14	9·061	0·697
Methyl citraconate . . .	13	8·364	
Ethyl fumarate . . .	13	10·112	0·487
Ethyl maleate . . .	15	9·625	
Ethyl chlorofumarate . .	—	11·377	0·462
Ethyl chloromaleate . .	—	10·915	

If the derivatives of maleic acid are compared with the
corresponding saturated compounds, it is seen that the effect
of unsaturation is approximately the same as that found with
ordinary monobasic acids, *e.g.*—

[1] Perkin, *Trans. Chem. Soc.*, **53**, 601 (1888); **69**, 1145 (1896).

Ethyl citraconate . . . . M = 10·517
Ethyl pyrotartrate . . . . M = 9·347

$$\overline{\qquad\qquad}$$

Unsaturation . . . . = + 1·170
Average value for unsaturation in carboxylic acids = + 1·154

The above table shows that the fumaroid compounds have the larger rotation and are therefore abnormal.

While considering stereo-isomerides we may turn for a moment to optical isomerides; and, as might be expected, we find that the magnetic rotatory powers of the inactive and active forms are almost the same.

Ethyl *d.* tartrate [1] . . . . . . M (15°) = 8·766
Ethyl *d. l.* tartrate [1] . . . . . M (16°) = 8·759
Dipentene [2] . . . . M (16°) = 11·315
d. Limonene [3] . . . . M = 11·246
d.l. $\Delta^{3\cdot8(9)}$ *p.* Menthadiene [2] . . . M (16°) = 12·939
d. $\Delta^{3\cdot8(9)}$ *p.* Menthadiene . . . M (13°) = 13·061

The values obtained by Perkin [4] for polyhydroxylic compounds show that in optically active substances the magnetic rotation is not influenced by the configuration; for example, we have—

Glucose . . . M = 6·723   Lactose . . M = 12·714
Galactose . . M = 6·887   Maltose . . M = 12·690

We see, then, that magnetic rotation is a highly constitutive property; but since the rotations of some of the isomeric esters quoted in Table III. are almost identical we may expect to find additive relations. The latter are not so well developed as with refractive power or molecular volume, but they can be clearly detected if we confine our attention to the simple compounds of the aliphatic series.

[1] Perkin, *Trans. Chem. Soc.*, **51**, 363 (1887).
[2] Perkin, *Trans. Chem. Soc.*, **89**, 849 (1906).
[3] Perkin, *Trans. Chem. Soc.*, **81**, 315 (1902).
[4] *Trans. Chem. Soc.*, **81**, 177 (1902).

§ 4. *HOMOLOGUES—THE VALUE OF THE METHYLENE GROUP*

The study of the additive relations is most conveniently begun by examining the effect of CH_2 on rotatory power in homologous series. Having obtained a value for the methylene group we may then proceed to resolve the rotation of any compound into the sum of the CH_2-effects and a residue which will represent the effect of the other groups in the molecule. Since the value of the methylene group is important it may be fully illustrated. The following table shows the molecular rotations (M) of several homologous series. The column under Δ shows the increase in molecular rotation caused by addition of CH_2 to the preceding compound, whilst under the heading S is shown the series-constant, a number which will be described in a subsequent paragraph.

TABLE VI.

HYDROCARBONS.

Substance.	Diff. in composition.	$M_t.$ [1]	Δ	S.
Pentane	CH_2	5·638		0·478
Hexane	CH_2	6·670	1·032	0·542
Heptane	CH_2	7·669	0·999	0·558
Octane [2]	CH_2	8·772	1·103	0·588
Decane [2]	$2CH_2$	10·998	$2 \times 1·113$	0·768
Isopentane	CH_2	5·750		
Isohexane		6·769	1·019	

HALOGEN DERIVATIVES.

Methyl iodide . . .	CH_2	9·009		7·986
Ethyl iodide	CH_2	10·075	1·066	8·029
Propyl iodide . . .	$5CH_2$	11·080	1·005	8·011
Octyl iodide		16·197	$5 \times 1·023$	8·013
Methyl bromide . . .	CH_2	4·644		(3·621)
Ethyl bromide . . .	CH_2	5·851	1·207	3·805
Propyl bromide . . .	$5CH_2$	6·885	1·034	3·816
Octyl bromide . . .		12·025	$5 \times 1·028$	3·841

[1] t varies between the extreme limits of $10°$ and $21°$.

[2] Schönrock, *Zeit. Phys. Chem.*, 11, 753 (1893).

TABLE VI.—*continued.*

Substance.	Diff. in composition.	M_{r}^{1}	Δ	S.
Ethyl chloride . . .	CH$_2$	4·039		1·993
Propyl chloride . . .		5·056	1·017	1·987
Octyl chloride . . .	5CH$_2$	10·128	5×1·014	1·944

ALCOHOLS.

Methyl alcohol . . .	CH$_2$	1·640		(0·617)
Ethyl alcohol . . .	CH$_2$	2·780	1·140	0·734
Propyl alcohol . . .	4CH$_2$	3·768	1·098	0·699
Heptyl alcohol . . .	CH$_2$	7·850	4×1·043	0·689
Octyl alcohol . . .		8·880	1·030	0·696

ALDEHYDES.

Acetaldehyde . . .	CH$_2$	2·385		(0·339)
Propaldehyde . . .	4CH$_2$	3·332	0·947	0·263
Heptylaldehyde . . .		7·422	4×1·022	0·261

KETONES.

Acetone	2CH$_2$	3·514		(0·445)
Methyl propyl ketone .	2CH$_2$	5·499	2×0·992	0·384
Dipropyl ketone. . .		7·471	2×0·986	0·310

ACIDS.

Formic acid	CH$_2$	1·671		(0·648)
Acetic acid	CH$_2$	2·525	0·854	(0·479)
Propionic acid . . .	CH$_2$	3·462	0·937	0·393
Butyric acid	CH$_2$	4·472	1·010	0·380
Valerianic acid . . .	2CH$_2$	5·513	1·041	0·398
Oenanthylic acid . .	CH$_2$	7·552	2×1·019	0·391
Caprylic acid . . .	CH$_2$	8·565	1·013	0·381
Pelargonic acid . . .		9·590	1·025	0·383

ACETIC ESTERS.

Methyl acetate . . .	CH$_2$	3·362		(0·293)
Ethyl acetate. . . .	CH$_2$	4·462	1·000	0·370
Propyl acetate . . .	5CH$_2$	5·487	1·025	0·372
Octyl acetate. . . .	8CH$_2$	10·601	5×1·023	0·371
Cetyl acetate . . .		18·772	8×1·021	0·358

ETHYL ESTERS OF FATTY ACIDS.

Ethyl propionate . .	CH$_2$	5·452		0·292
Ethyl butyrate . .	2CH$_2$	6·477	1·025	0·339
Ethyl caproate . . .	CH$_2$	8·509	2×1·016	0·325
Ethyl oenanthylate . .	2CH$_2$	9·541	1·032	0·334
Ethyl nonylate . . .		11·571	2×1·015	0·318

On examining the column under Δ it is seen that the addition of CH_2 causes an approximately constant increase in molecular rotation, and this increase is very nearly the same in different classes of compounds. Perkin has calculated the average value for CH_2 from a wider range of material, and he found that

$$CH_2 = 1\cdot023$$

It may be remarked that the initial members in many of the series are not in harmony with the derivatives of higher molecular weight, since they give slightly abnormal values for the CH_2 difference and series constant. This behaviour, as we have previously noticed, may be caused by association which would reduce the molecular rotatory power,[1] or perhaps by the lack of strict analogy between the constitution of the simple bodies and the higher derivatives. With regard to the latter circumstance it should be noted that in the first member of a series—say methyl alcohol CH_3OH—carbon is united to hydrogen and oxygen, so that on passing to the next substance—ethyl alcohol $CH_3 . CH_2 . OH$—the effect of homology is measured for CH_2 united to one carbon atom. But the second homologous step—to propyl alcohol $CH_3CH_2CH_2OH$—is somewhat different, being formed by adding carbon united to two other carbon atoms; and since magnetic rotation is very sensitive to constitutive influences, we must expect these dissimilar structural changes to have correspondingly unequal effects on the rotation. It will be remembered that the abnormal value of the initial methylene group can also be traced in the refractive power.

With the aid of the value for CH_2 it is possible to calculate the molecular rotation of any member of an homologous series if the rotation of one of the members has been accurately determined. Thus—

Methyl iodide, CH_3I . . . . . $M = 9\cdot009$
Hence for octyl iodide, $C_8H_{17}I$. $M = 9\cdot009 \times 7 \times 1\cdot023$
$\qquad\qquad\qquad\qquad\qquad\qquad = 16\cdot17$ appxt.
Experiment gives for octyl iodide $\quad M = 16\cdot20$ appxt.

[1] Perkin, *Trans. Chem. Soc.*, **69**, 1071 (1896).

The Series Constant.—If there are nCH$_2$ groups in a compound whose molecular rotation is M, then the expression

$$M - n(1 \cdot 023) = S$$

represents the rotatory effect of the remainder of the molecule. The numbers under S in the foregoing tables show the value of this expression for each substance, and it will be seen that S is approximately constant for all the higher members of a given series. This is called the series constant. The annexed table contains the constants calculated by Perkin [1] from a large collection of data. If a substance does not contain carbon and hydrogen in the atomic proportion C : 2H, the series constant is obtained by subtracting from the molecular rotation the value of $n \times 1 \cdot 023$, where n is the total number of carbon atoms in the compound. It will be noticed that under these circumstances the series constant has a somewhat different meaning.

TABLE VII.

Series.	Empirical formula.	S+n . CH$_2$.
Paraffins (normal) . . .	C_nH_{2n+2} . .	$0 \cdot 508 + n \times 1 \cdot 023$
Alcohols	$C_nH_{2n+1}OH$.	$0 \cdot 699 +$,,
Aldehydes	$C_nH_{2n}O$ . . .	$0 \cdot 261 +$,,
Ketones	$C_nH_{2n}O$ . . .	$0 \cdot 375 +$,,
Acids	$C_nH_{2n}O_2$ . . .	$0 \cdot 393 +$,,
Esters of formic acid . .	$C_nH_{2n}O_2$ . . .	$0 \cdot 495 +$,,
Esters of acetic acid . .	$C_nH_{2n}O_2$ . . .	$0 \cdot 370 +$,,
Esters of higher acids . .	$C_nH_{2n}O_2$ . . .	$0 \cdot 337 +$,,
Methyl esters of acids . .	$C_nH_{2n}O_2$ . . .	$0 \cdot 273 +$,,
Ethyl esters of acids. . .	$C_nH_{2n}O_2$ . . .	$0 \cdot 337 +$,,
Chlorides	$C_nH_{2n+1}Cl$ . .	$1 \cdot 988 +$,,
Bromides	$C_nH_{2n+1}Br$ . .	$3 \cdot 816 +$,,
Iodides	$C_nH_{2n+1}I$ . .	$8 \cdot 011 +$,,

We may thus write a general formula for the rotation of any series

$$M = S + n \times 1 \cdot 023$$

[1] Perkin, *Trans. Chem. Soc.*, **45**, 574 (1884).

e.g. for the fatty acids

$$M = 0\cdot393 + n \times 1\cdot023$$

or for alkyl bromides

$$M = 3\cdot816 + n \times 1\cdot023$$

Having found the series constants for a number of compounds, it is often possible to calculate the molecular rotation of a more complicated substance with some degree of accuracy. The process [1] is based on the assumption that the series constant of a complex substance is approximately the arithmetic mean of the constants of the simpler types from which it is derived. We may thus calculate the series constant of the substance in question, and from this the molecular rotation can be obtained by adding as many times $1\cdot023$ (CH_2) as the compound contains carbon atoms. The following examples illustrate the process.

Ethyl tartrate, $C_2H_5OOC \cdot CHOH \cdot CHOH \cdot COOC_2H_5$

Glycol, series constant = $0\cdot897$
Ethyl succinate, series constant = $0\cdot196$

$$\text{sum} = 1\cdot093$$

Hence series constant of ethyl tartrate = $1\cdot093 \div 2 = 0\cdot546$
adding $8 \times 1\cdot023 = 8\cdot184$

Calculated molecular rotation of ethyl tartrate = $8\cdot730$

Found by experiment = $8\cdot766$

Ethyl lactate, $CH_3CHOHCOOC_2H_5$
Secondary alcohol, series constant = $0\cdot844$
Ethereal salt, series constant = $0\cdot337$

$$1\cdot181$$

Ethyl lactate, calculated series constant = $0\cdot590$
add $5 \cdot CH_2 = 5\cdot115$

Molecular rotation of ethyl lactate (calc.) = $5\cdot705$

Found by experiment = $5\cdot720$

[1] Perkin, *Trans. Chem. Soc.*, **61**, 805 (1892).

This process of calculating the molecular rotation of a substance is called the series constant method; and we shall later find occasion to employ it in dealing with the applications of this property to problems of structure.

§ 5. *THE RELATIONS BETWEEN TWO SERIES*

Replacements.—If we compare the molecular rotatory powers of two substances which are related to one another by the replacement of an atom or group, we obtain the rotatory effect of the displacement. The effect on rotatory power of a given change in structure is by no means constant for all types of substances, since the rotatory value of a replacement depends on the composition and structure of the parent compound. With homologues the effect of the displacement is approximately constant; thus, on comparing the rotations of the normal alkyl chlorides and bromides, we see that the effect of exchanging chlorine for bromine in the

Ethyl derivative is $+1\cdot 812$
In the propyl derivative is $+1\cdot 829$
And in the octyl derivative is $+1\cdot 897$

In simple cases like the above we may obtain the average effect of the replacement by comparing the series constants with one another.

e.g. series constant alkyl bromides $(n CH_2 + HBr) =$ $3\cdot 816$
     „   „   chlorides $(n CH_2 + HCl) =$ $1\cdot 988$
                              hence Cl by Br $= +1\cdot 828$

Similarly we have Cl by I $= +6\cdot 020$
        H by Cl $= +1\cdot 480$
        H by Br $= +3\cdot 308$
        H by I $= +7\cdot 503$

Other replacements may be calculated from the series of constants given in Table VII.

If now we calculate the values of a given displacement in

different classes of compounds, we no longer obtain a constant effect as with homologous compounds. For example—

Allyl bromide . M = 8·221 Propyl bromide . M = 6·885
Allyl chloride . M = 6·008 Propyl chloride . M = 5·056

Exchange of Cl for Br = +2·213 or, +1·829.

n. Octane . . M = 8·722 Ethyl propionate. M = 5·452
n. Octyl alcohol. M = 8·880 Ethyl lactate . . M = 5·720

Exchange of H for OH = + 0·158, or +0·268.

This may be further illustrated by repeating a displacement in the same molecule, when it is seen that the successive changes vary in their rotatory effects. The halogen deriva-tives[1] of the fatty acids may be employed as examples.

TABLE VIII.

	M.	H by Cl.		M.	H by Br.
Acetic acid . . .	2·525		Acetic acid . . .	2·525	
Chloracetic acid . .	3·888	1·363	Bromacetic acid. .	5·601	3·076
Dichloracetic acid .	5·293	1·405	Dibromacetic acid .	8·738	3·137
Trichloracetic acid .	6·458	1·165	Tribromacetic acid .	12·152	3·414
Ethyl acetate . . .	4·462		Ethyl acetate . .	4·462	
Ethyl chloracetate .	5·846	1·384	Ethyl bromacetate .	7·609	5·147
Ethyl dichloracetate .	7·313	1·467	Ethyl dibromacetate	10·732	3·123
Ethyl trichloracetate .	8·494	1·181	Ethyl tribromacetate	14·320	3·588

For obvious reasons, we may dispense with a detailed examination of the numerous replacement-values which might be calculated from the data collected by Perkin; but for the convenience of the reader who may require to do this for any particular case, the references to various classes of compounds are collected at the foot of the page.[2] There are, however, two

[1] Perkin, *Trans. Chem. Soc.*, **65**, 407 (1894).

[2] Hydrocarbons, alkyl mono and polyhalides, alcohols, aldehydes, ketones, ethers, esters of mono and dibasic acids, acids, and unsaturated compounds, *Trans. Chem. Soc.*, **45**, 575 (1884); unsaturated acids, *Trans. Chem. Soc.*, **53**, 661, 695 (1888); nitrogen compounds, amines, nitrates, nitro compounds, etc., *Trans. Chem. Soc.*, **55**, 748 (1889); halogen acids,

structural changes which are of peculiar interest, and we shall consider these in detail.

§ 6. UNSATURATION[1] AND RING-FORMATION[2]

Unsaturated compounds have always a greater rotation than the corresponding saturated substances; but the difference between the two series—or the effect of unsaturation—is not always the same. This may be illustrated by the examples quoted in the following table, which shows the effect of changing the saturated to ethylenic structure. We shall return to these substances in a subsequent portion of this chapter, but for the present it is sufficient to observe that the examples may be separated into two groups, in one of which the effect of unsaturation is about 0·9 or below, and in the other about 1·1 or above.

The value is lowest in the hydrocarbons and highest in the esters of the dibasic acids quoted. Perkin assumes the average value for unsaturation in the esters of carboxylic acids to be + 1·112.

TABLE IX.

ETHYLENE DERIVATIVES.

Substance.	Formula.	M.	Effect of unsaturation.
Hexane	$CH_3(CH_2)_4CH_3$	6·670	+0·803
Hexylene	$CH_2CH_2CH_2CH=CH.CH_3$ . .	7·473	
Diallyl	$CH_2=CH—CH_2CH_2—CH=CH_2$	8·420	+0·947
Octane	$CH_3(CH_2)_6CH_3$	8·722	+0·684
Octylene	$CH_3(CH_2)_5CH=CH_2$	9·406	
Isopentane	$CH_3CH_2CH(CH_3)_2$	5·750	+0·444
Amylene	$CH_3—CH=C(CH_3)_2$	6·194	
Hexamethylene . .	⬡	5·664	+0·728
Tetrahydrobenzene .	⬡	6·392	

Trans. Chem. Soc., **65**, 402 (1894) ; aromatic compounds, *Trans. Chem. Soc.*, **69**, 1236 (1896).

[1] Perkin, *Trans. Chem. Soc.*, **45**, 561 (1884); **49**, 205 (1886); **67**, 261 (1895) ; **91**, 835, 851 (1907).

[2] Perkin, *Trans. Chem. Soc.*, **81**, 292 (1902).

TABLE IX.—*(continued)*.

Substance.	Formula.	M.	Effect of unsaturation.
1 Dimethyl hexahydrobenzene	(hexagon)$(CH_3)_2$	8·150	+0·753
1 Dimethyl Δ^3 tetrahydrobenzene	(hexagon with double bond)$(CH_3)_2$	8·903	
Laurolene	$(CH_3)_2$ (pentagon) $. CH_3$	8·749	+0·500
Dihydrolaurolene	$(CH_3)_2$ (pentagon) $. CH_3$	8·249	
Propyl chloride	$CH_3CH_2CH_2Cl$	5·056	+0·952
Allyl chloride	$CH_2{=}CH{-}CH_2Cl$ . . .	6·008	
Propyl alcohol	$CH_3CH_2CH_2OH$	3·768	+0·914
Allyl alcohol	$CH_2{=}CH{-}CH_2OH$ . . .	4·682	
Valerianic acid	$CH_3{-}(CH_2)_3COOH$ . .	5·513	+0·913
Allyl acetic acid	$CH_2{=}CH{-}(CH_2)_2COOH$ . .	6·426	
Propyl malonic ester	$CH_3CH_2CH_2{-}CH(COOEt)_2$ . .	10·367	+0·914
Allyl malonic ester	$CH_2{=}CH{-}CH_2{-}CH(COOEt)_2$.	11·281	
Undecylic acid	$CH_3{-}CH_2(CH_2)_8COOH$ . . .	11·641	+0·906
Undecylenic acid	$CH_2{=}CH(CH_2)_8COOH$ . .	12·547	
Caprylic acid	$CH_3(CH_2)_6CH_2COOH$	8·565	2×+0·890
Diallyl acetic acid	$(CH_2{=}CH{-}CH_2)_2CH . COOH$.	10·344	
Ethyl butyrate	$CH_3CH_2CH_2COOEt$	6·477	+1·112
Ethyl crotonate	$CH_3CH{=}CHCOOEt$ . . .	7·589	
Ethyl succinate	$COOEtCH_2CH_2COOEt$ . . .	8·380	+1·245
Ethyl maleate	$COOEtCH{=}CHCOOEt$ . . .	9·625	
Ethyl pyrotartrate	$COOEtCH{-}CH_2COOEt$ CH_3	9·347	+1·120
Ethyl itaconate	$COOEtC{-}CH_2COOEt$ $\|CH_2$	10·467	
Ethyl pyrotartrate	$COOEtCH{-}CH_2COOEt$ CH_3	9·347	+1·170
Ethyl citraconate	$COOEtC{=}CHCOOEt$ CH_3	10·517	
methyl ethyl isobutyl ketone	$CH_3CO{-}CH_2{-}CH(CH_3)_2$	6·612 (calc.)[1]	+1·166
Mesityl oxide	$CH_3CO{-}CH{=}C(CH_3)_2$ . . .	7·778	
Ethyl stearate	$CH_3(CH_2)_{16}COOEt$ . . .	20·785	+1·124
Ethyl oleate	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOEt$	21·909	

[1] Calculated thus: series const. ketones (0·364)+6CH₂ (6·138)+iso-grouping (110) = 6·612.

A few acetylene derivatives have been investigated, and these are compared with the saturated derivatives in the next list.

TABLE X.

Substance.	Formula.	M.	Effect of unsaturation.
Methyl *n*. butyl ketone.	$CH_3CH_2CH_2CH_2COCH_3$	6·522 [1]	+0·657
Methyl Δ^γ butinene ketone	$CH \equiv C—CH_2CH_2COCH_3$	7·179	
Ethyl valerianate . .	$CH_3CH_2CH_2CH_2COOEt$	7·500	+0·629
Ethyl Δ^γ butinene *a* carboxylate	$CH \equiv CHCH_2CH_2COOEt$	8·129	
Propionic acid : . .	CH_3CH_2COOH . . .	3·462	+0·779
Propiolic acid . . .	$CH \equiv C . COOH$ . . .	4·241	
Ethyl propionate . .	CH_3CH_2COOEt . . .	5·452	+0·859
Ethyl propiolate . .	$CH \equiv C . COOEt$ . . .	6·311	

It may be observed that to obtain the increment due to unsaturation of the two carbon atoms in the ethylenic linkage

$$H {>} C—C {<} H \longrightarrow {>} C = C {<}$$
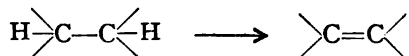
we must add to the values quoted in the tables the effect of the hydrogen atoms $(H_2 = + 0.508)$ which are removed during the process of unsaturation.

Turning to *ring-formation*, we find that if a saturated open chain is converted to a cyclic arrangement by removal of two hydrogen atoms, there is a *decrease* in magnetic rotatory power, and, as with unsaturation, the effect does not preserve a strictly constant value in different classes of compounds. We may at once proceed to consider the data which illustrate this rule (see Table XI., p. 477).

It is doubtful whether the first two comparisons on the list are legitimate, for we are here comparing the higher members of the open-chain series with the initial members of the cyclo-paraffin acids. Perkin recommends that the comparison should be made between substances whose position in each series is

[1] Calculated from methyl propyl ketone (5·499), and CH_2 (1·023).

TABLE XI.—RING-FORMATION.

Substance.	Formula.	M.	Effect of ring-formation.
Butyric acid. . .	$CH_3CH_2CH_2COOH$	4·472	−0·331
Trimethylene carb-oxylic acid	$C_3H_5 . COOH$	4·141	
Valerianic acid . .	$CH_3CH_2CH_2CH_2COOH$	5·513	−0·465
Tetramethylene carb-oxylic acid	$C_4H_7 . COOH$	5·048	
Hexylic acid . .	$CH_3(CH_2)_4COOH$	6·530	−0·639
Pentamethylene carb-oxylic acid	$C_5H_9 . COOH$	5·891	
Octylic acid . . .	$CH_3(CH_2)_6COOH$	8·580	−0·605
Methyl hexamethy-lene carboxylic acid	$HOOCCH \overset{\overset{\displaystyle CH_2\ \ CH_2}{\diagup\ \ \ \ \ \diagdown}}{\underset{\underset{\displaystyle CH_2\ \ CH_2}{\diagdown\ \ \ \ \ \diagup}}{\ \ \ \ \ \ \ }} HCCH_3$	7·975	
Iso-octane . . .	$(CH_3)_3C . CH_2CH_2CH_2CH_2CH_3$	8·828 [1]	−0·678
1.1. Dimethyl cyclo-hexane	$(CH_3)_2{=}\hexagon$	8·150	
Iso-octane . . .	$(CH_3)_3C . CH_2CH_2CH_2CH_2CH_3$	8·828	−0·579
Dihydroisolaurolene	$(CH_3)_2{=}\underset{\displaystyle CH_3}{\pentagon}$	8·249	
n. Hexane . . .	$CH_3CH_2CH_2CH_2CH_2CH_3$	6·646	−0·982
Cyclohexane . .	C_6H_{12}	5·664	
Methyl butyl ketone	$CH_3COCH_2CH_2CH_2CH_3$	6·522 [2]	−0·621
Methyl cyclobutyl ketone	$CH_3CO\diagdown\underset{\displaystyle CH-CH_2}{\overset{\displaystyle CH_2-CH_2}{\ \ \ \ |\ \ \ \ \ \ |}}$	5·901	
Ethyl butyl ketone .	$C_3H_5CO(CH_2)_3CH_3$	7·545 [3]	−0·634
Ethyl cyclobutyl ketone	$C_2H_5CO-\underset{\underset{\displaystyle CH_2-CH_2}{|\ \ \ \ \ \ |}}{CH-CH_2}$	6·911	

[1] Calculated from octane (8·722) + iso formation (+ 0·106) = 8·828.

[2] Calculated from methyl propyl ketone (5·499) + CH_2 (1·023) = 6·522.

[3] Calculated from methyl propyl ketone.

much the same; that is, trimethylene carboxylic acid must be compared with formic acid, tetramethylene carboxylic acid with acetic acid, and so on. On making allowance for the requisite number of methylene groups in the fatty acids, the comparisons would be as shown in the annexed list; and it will be seen that the concordance in the values of ring-formation is certainly better.

TABLE XII.

Formic acid + 3CH$_2$ = 1·671 + 3·069 . . = 4·740	−0·599
Trimethylene carboxylic acid . . . . = 4·141	
Acetic acid + 3CH$_2$ = 2·525 + 3·069 . . = 5·594	−0·546
Tetramethylene carboxylic acid . . . = 5·048	
Propionic acid + 3CH$_2$ = 3·462 + 3·069 . . = 6·531	−0·640
Pentamethylene carboxylic acid . . . . = 5·891	
Valerianic acid + 3CH$_2$ = 5·513 + 3·069 . . = 8·582	−0·607
Methylhexamethylene carboxylic acid . . = 7·975	

Adopting this method of comparison, we may conclude that the value of ring-formation lies in the neighbourhood of −0·6 units; but the abnormally high effect with cyclo-hexane should be observed. For this reason it is perhaps premature to accept this value for ring-formation as definitely established; but it may be noted that similar results are obtained from bicyclic compounds. Thus the bicyclic ketone—camphor— has the structure

$$
\begin{array}{ccccc}
CH_2 & \!\!\!\!-\!\!\!\! & CH & \!\!\!\!-\!\!\!\! & CH_2 \\
| & & | & & | \\
& & CH_3 \cdot C \cdot CH_3 & & \\
| & & | & & | \\
CH_2 & \!\!\!\!-\!\!\!\! & C & \!\!\!\!-\!\!\!\! & CO \\
& & | & & \\
& & CH_3 & &
\end{array}
$$
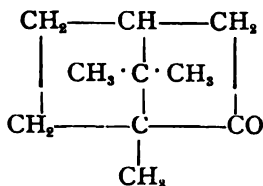
C$_{10}$H$_{16}$O, Camphor.   M = 9·265.

and the formula of the corresponding open-chain saturated ketone would be C$_{10}$H$_{20}$O. The rotation of the latter may be derived from that of methyl hexyl ketone C$_8$H$_{16}$—

$$\text{Methyl hexyl ketone} = 8\cdot509$$
$$2CH_2 = 2\cdot046$$
$$\text{hence } C_{10}H_{20}O = 10\cdot555$$

This value for the open-chain compound exceeds that found for camphor ($9\cdot265$) by $1\cdot290$, whence it follows that the formation of one ring depresses the rotatory power by $1\cdot290 \div 2$, or $0\cdot645$ units. Also with borneol
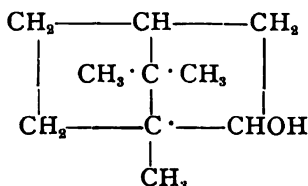
Borneol, $C_{10}H_{18}O$.

we have $M = 9\cdot807$, whereas by calculation for the secondary alcohol $C_{10}H_{22}O$

$$\text{sec. Octyl. alcohol} = 9\cdot034$$
$$CH_2 \times 2 = 2\cdot046$$
$$\text{open-chain alcohol } C_{10}H_{22}O = 11\cdot080$$

whence the value for double-ring formation is $-1\cdot273$ and for one ring $-0\cdot636$.

§ 7. THE CALCULATION OF MAGNETIC ROTATORY POWER

From the results obtained with homologues and displacements, we see that magnetic rotation is a highly constitutive property; but fortunately the additive relations are sufficiently well defined to enable them to be used in calculating the unknown rotation of a substance. We have already considered the method based on the " series constants," and it may now be observed that also the replacement-values may be employed for this purpose. The process, which may be called the displacement method, is very simple. If the rotation of a

complex substance is required, we must first obtain the experimental value of a compound which can be converted into it by simple replacements or structural changes; the rotation of the parent substance is then modified according to these changes. Since it is impossible to assign a general value to any replacement, care must be taken to employ values which have been obtained from compounds of closely allied constitution, otherwise the result may be very inaccurate. The following examples serve to illustrate the process, and to show the degree of accuracy of the results.

ETHYL TRICHLOROLACTATE, $CCl_3CHOHCOOC_2H_5$

$$
\begin{array}{rr}
\text{Trichloracetic acid} = & 6\cdot458 \\
\text{Acetic acid} = & 2\cdot525 \\
\hline
\text{3H by 3Cl} = & +3\cdot933 \\
\text{Ethyl lactate} = & 5\cdot720 \\
\hline
\text{Hence ethyl trichlorolactate} = & 9\cdot653 \\
\text{Experiment gave M} = & 9\cdot361 \\
\end{array}
$$

ETHYL ESTER OF DIETHYLACETOACETIC ACID

$$CH_3COC(C_2H_5)_2COOC_2H_5$$

We must first calculate the rotation of the ketonic form of acetoacetic ethyl ester.

$$
\begin{array}{rr}
\text{Ethyl pyruvate} = & 5\cdot504 \\
\text{Ethyl propionate} = & 5\cdot452 \\
\hline
\text{H}_2 \text{ by O} = & +0\cdot052 \\
\end{array}
$$

Then since

$$\text{Ethyl butyrate} = 6\cdot477$$
we have Ethyl acetoacetate $= 6\cdot477 + 0\cdot052 = 6\cdot529$
but Ethyl diethylmalonate $= 11\cdot197$
whilst Ethyl malonate $= 7\cdot410$

hence $H_2C< \;\rightarrow\; (C_2H_5)_2C< \;= +3\cdot787$

[1] Experiment gave M $= 6\cdot501$, see p. 503.

And finally—

Ethyl diethylacetoacetate $= 6\cdot529 + 3\cdot787 = 10\cdot316$
whilst experiment gave $M = 10\cdot115$

ETHYLIDENE GLYCOL $CH_3CH(OH)_2$

Chloral $CCl_3CHO =$	$6\cdot591$
Chloral hydrate $CCl_3CH(OH)_2 =$	$7\cdot037$

hence $—CHO \rightarrow —CH(OH)_2 = + 0\cdot446$

and since Acetaldehyde $CH_3CHO =$ $2\cdot385$
M for Ethylidene glycol would be $=$ $2\cdot831$

These methods of calculation are important, since they afford a means of determining the constitution of a substance. In order to do this a previous knowledge of the possible structures is required, and then the calculated value for each possibility may be compared with the experimental rotation. The substance may be considered to have that structure which most closely accords with the experimental result. It should be observed that in applying this method of determining constitution the theoretical values should be calculated in as many ways as possible. As an example we may take levulinic acid.

LEVULINIC ACID.

Ketonic form, $CH_3COCH_2CH_2COOH.$

I.

Pyruvic acid	$3\cdot557$
Propionic acid	$3\cdot462$
Replacement of H_2 by O . . . $= +0\cdot095$	
But valerianic acid	$5\cdot513$
Hence $CH_3COCH_2CH_2COOH$. $=$	$5\cdot608$

II.

Series const. of acids ($C_nH_{2n}O_2$) . . $= 0\cdot393$
Series const. of ketones . . . . . $= 0\ 375$

Hence *s.* for ketonic acids . . . . $= 0\cdot384$
Then adding $5 \times 1\cdot023$ . . . . . $= 5\cdot115$

We have $CH_3COCH_2CH_2COOH$ . . $= 5\cdot499$

Enolic form, $CH_3C(OH)=CHCH_2COOH$.

I.

Ethyl lactate . . . . $5\cdot720$
Ethyl propionate . . . . $5\cdot452$

Hence H by OH . . . . $+0\cdot268$
Then since valerianic acid . . . . . $5\cdot513$

γ oxyvalerianic acid . . . . $5\cdot781$
But unsaturation . . . . $+1\cdot112$

Hence $CH_3C(OH)=CHCH_2COOH$. $= 6\cdot893$

II.

Ethyl crotonate . . . . $7\cdot589$
H by OH (as before) . . . . . . $+0\cdot268$

Hence ethyl oxycrotonate . . . . . $7\cdot857$
Subtracting $2CH_2$ . . . . $2\cdot046$

Oxycrotonic acid . . . . $5\cdot811$
Adding CH_2 . . . . $1\cdot023$

$CH_3C(OH)=CH\ .\ CH_2COOH$ . . $= 6\cdot834$

Since experiment gave for levulinic acid $M = 5\cdot509$, it follows that the acid has the ketonic structure.

The values of some of the elements and a few groups may be obtained, and they may be occasionally employed in calculating a rotation; but their use is very limited, and they should only be employed when other methods are unavailable.

The series constant 0·508 of the normal paraffins C_nH_{2n+2} is obtained by subtracting the value of nCH_2 from the rotation of any member of the series. This residue must represent the value for 2H, since $C_nH_{2n+2} - nCH_2 = 2H$. Hence we may write $2H = 0·508$, or the value of hydrogen as 0·254. Then again, it is known that $CH_2 = 1·023$, whence by deducting the value of 2H we may obtain the value for carbon = 0·515. Also the value of oxygen may be obtained by consideration of the fact that when hydrogen is replaced by hydroxyl, a rise in rotation of 0·191 units takes place. This replacement consists simply of the addition of oxygen, whose value may therefore be taken as + 0·191.

Again, when hydrogen is removed from a compound and replaced by chlorine, there is an increase in rotatory power of 1·480; hence the value for chlorine may be assumed to be $1·480 + 0·254 = 1·734$. Similarly, bromine and iodine may be calculated to be equivalent to 3·562 and 7·757 respectively. Humburg [1] has found the values for chlorine and bromine to be 1·675 and 3·563.

These and a few other values [2] are collected in the annexed table.

TABLE XIII.

Element.	Observed by—	
	Perkin.	Humburg.
H	0·254	—
C=O (ketones). . .	0·850	—
O (in OH)	0·191	—
C=O (aldehydes) . .	0·776	—
C	0·515	—
Br	3·562	3·563
Cl.	1·734	1·675
I	7·757	—
NO$_2$	0·483	—
N^{III} (in amines) . .	0·717	—

[1] *Zeit. Phys. Chem.*, **12**, 401 (1893).

[2] Perkin, *Trans. Chem. Soc.*, **55**, 753 (1889); **67**, 255 (1895); **69**, 1025 (1896); **81**, 292 (1902).

§ 8. *MAGNETO-OPTICAL EXALTATION*

We have seen in the chapter dealing with refractivity that when unsaturated atoms are united, the molecular refractive power of the compound assumes a greater value than that calculated from the sum of the refractive effects. It is interesting to find that a similar anomaly is shown by magnetic rotation; but we may here observe that the parallel between the two is not strict. As yet the relations between magnetic rotation and conjugation of unsaturated groups in aliphatic compounds have not been very thoroughly investigated, but the examples collected by Perkin[1] are sufficient to afford a general illustration. If we compare hydrocarbons containing the conjugated system —CH=CH—CH=CH— with the corresponding saturated compounds, we see that the average effect of each unsaturation is much greater than that observed with hydrocarbons containing a single ethylenic linkage. From the examples already given[2] to show the effect of unsaturation, it is evident that the introduction of a single ethylenic linkage in the hexamethylene system causes a rise in rotation of about 0·73 units; but comparing $\Delta^{1.3}$ dihydrobenzene with hexamethylene, it is seen that

$\Delta^{1.3}$ Dihydro benzene   M = 8·093

Hexamethylene   M = 5·664
                                    _____
                                    2·429
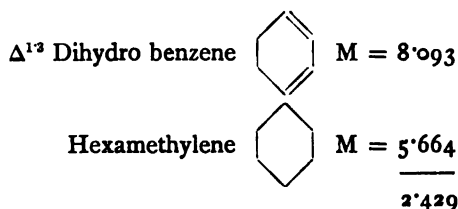
the combined effect of two conjugated ethylene bonds is 2·429, or an average for each of 1·214. Similarly with
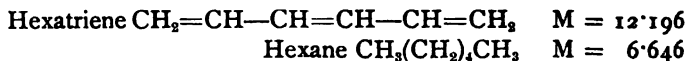
Hexatriene CH$_2$=CH—CH=CH—CH=CH$_2$ M = 12·196
Hexane CH$_3$(CH$_2$)$_4$CH$_3$ M = 6·646
                                            _____
Effect of triple conjugated unsaturation =   5·550
or for one unsaturation =   1·850

[1] *Trans. Chem. Soc.*, **89**, 854 (1906); **91**, 806 (1907).
[2] Table IX., p. 474.

and with

d.l. $\Delta^{3(8)\cdot9}$ *p.* Menthadiene, CH_3⟨ring⟩—C⟨$^{CH_2}_{CH_3}$ M = 12·939

p. Menthane * CH_3⟨ring⟩—HC⟨$^{CH_3}_{CH_3}$ M = 9·862
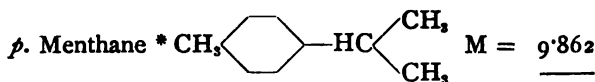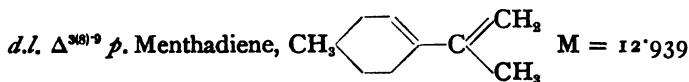
$$\text{Effect two conjugated ethylenic bonds} = 3\cdot077$$
$$\text{or one ethylenic bond} = 1\cdot538$$

This "exalted" effect of unsaturation can be further detected by comparing

Hexatriene $CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$ M = 12·196

with

Diallyl $CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$ M = 8·420
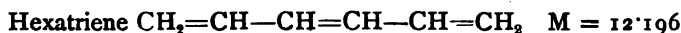
$$\text{whence effect of unsaturation} = 3\cdot776$$

And

d. $\Delta^{3(8)\cdot9}$ *p.* Menthadiene, CH_3⟨ring⟩—C⟨$^{CH_2}_{CH_3}$ M = 13·061

with

d. Limonene, CH_3⟨ring⟩—C⟨$^{CH_3}_{CH_2}$ M = 11·246
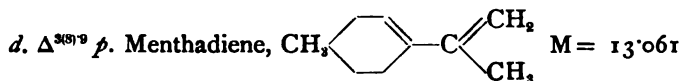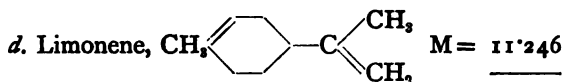
$$\text{whence the effect of conjugation} = +1\cdot815$$

In dipentene (*d.l.* limonene), where the ethylenic linkages are not in the conjugated position, the unsaturation has a normal value :

* Calculated thus—

$$\text{Hexamethylene} = 5\cdot664$$
$$4CH_2 = +4\cdot092$$
$$\text{Iso arrangement} = +0\cdot106$$
$$\text{Hence } p. \text{ menthane} = 9\cdot862$$

Dipentene, CH_3 [structure with ring and C bearing CH_2 and CH_3] $M = 11\cdot315$

p. Menthane, CH_3 [structure with ring and C bearing CH_3 and CH_3] M (calc.) $= 9\cdot862$

$$\text{hence double unsaturation} = 1\cdot453$$
$$\text{or unsaturation} = 0\cdot726$$
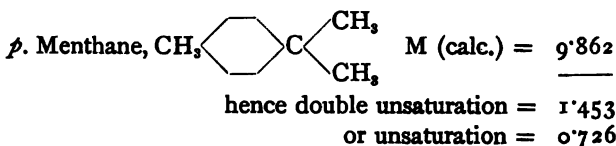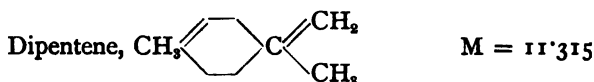
which approximates to the value already noticed with singly unsaturated hexamethylene derivatives. Turning back to the table illustrating the effect of unsaturation, we see that the examples may be placed in two classes, according to whether the effect is about $0\cdot9$ and less, or about $1\cdot1$ units and greater. Now it will be observed that the members of the former class either contain only one unsaturated group, or if they contain two these are isolated, whilst the latter division[1] includes substances derived from the type—

$$-HC{=}CH-\overset{|}{C}{=}O$$
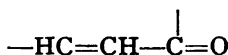
in which we have a conjugated system. Thus we again find that two contiguous unsaturated groups produce an abnormally high magnetic rotation. Reference to the table of acetylene derivatives will further show that acetylenic unsaturation varies from about $0\cdot65$ when isolated to $0\cdot8$ units when conjugated, *e.g.*—

Ethyl propionate $\rightarrow$ Ethyl propiolate $= + 0\cdot859$
CH_3CH_2COOEt $CH{\equiv}C.COOEt$

whilst

Ethyl valerianate $\rightarrow$ Ethyl Δ^γ butinene carboxylate
$= +0\cdot629$
$CH_3CH_2CH_2CH_2COOEt$ $CH{\equiv}C.CH_2CHCOOEt$
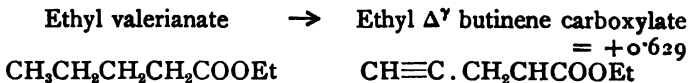
[1] It must be admitted that oleic acid, according to the comparison with the calculated value for ethyl stearate, is exceptional; but perhaps this is due to the accumulation of errors in calculating the rotation of a substance of such high molecular weight.

It is worth observing that the magneto-optical anomaly does not entirely disappear when the unsaturated groups are separated; it seems that the screening effect of intervening saturated groups is not sufficient to prevent the unsaturated complexes from influencing one another. Thus we find that the effect of unsaturation in the carboxylic acids, even though it be in the $\Delta^{3\cdot4}$ position, as with

Propyl malonic ester   →   Allyl malonic ester   + 0·914
$CH_3CH_2CH_2CH(COOEt)_2$ $CH_2=CHCH_2CH(COOEt)_2$
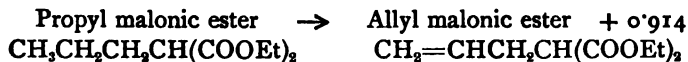
or in the $\Delta^{9\cdot10}$ position, as with

Undecylic acid   →   Undecylenic acid   + 0·906
$CH_3CH_2(CH_2)_3COOH$ $CH_2=CH(CH_2)_8COOH$
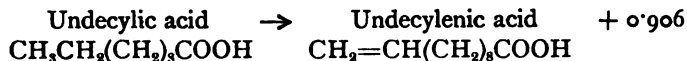
is always greater than with the singly unsaturated hydrocarbons, where the average effect is about 0·7 units.

The second unsaturation of diallyl also has a greater effect than the first :

Hexane   →   Hexylene   + 0·80
$CH_3(CH_2)_4CH_3$ $CH_3(CH_2)_2CH=CH . CH_3$
Hexylene   →   Diallyl   + 0·94
$CH_3(CH_2)_2CH=CHCH_3$ $CH_2=CH—CH_2—CH_2CH=CH_2$
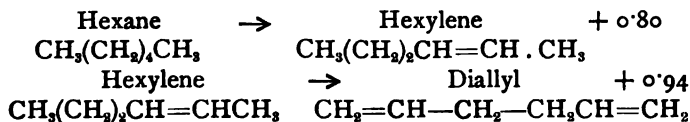
In this respect magneto-optical anomaly is a more sensitive indicator of conjugation than the simple optical anomaly which, it will be remembered, disappears when the unsaturated groups are isolated by a single methylene group.

The effect of conjugation is yet more prominently marked in aromatic compounds, in which the unsaturated benzene complex is united to other groups possessing residual affinity.

§ 9. *AROMATIC COMPOUNDS*[1]

We may begin the study of the group with the parent substance : benzene. The rotation of this compound exceeds

[1] Perkin, *Trans. Chem. Soc.*, **69**, 1025 (1896) ; **91**, 810 (1907).

that of cyclohexane by almost the same amount as the difference between hexatriene and hexane :

Benzene	. . $M_{15}° = 11\cdot284$	Hexatriene . . $M = 12\cdot196$
Cyclohexane	. $M_{15}° = 5\cdot664$	Hexane . . . $M = 6\cdot646$
	Difference $= 5\cdot620$	Difference $= 5\cdot550$

At first sight it might be supposed that this circumstance clearly points to the presence of three conjugated ethylene linkages in benzene. If, however, the structures of hexatriene and benzene be more closely examined, it is seen that the

$$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$$

Hexatriene.   Benzene (Kekulé).
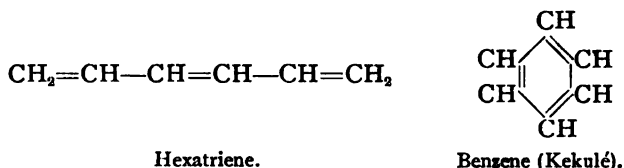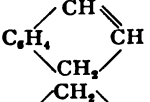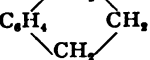
former substance contains a very different type of conjugation from that expressed by the Kekulé formula for benzene. In the latter there are three conjugated systems of the type—

$$-HC{=}CH{-}CH{=}CH-$$

whilst in hexatriene there are merely two such systems. From numerous examples which may be found among the data quoted in this chapter, it may be shown that increase in the complexity of conjugation increases the exaltation; hence it is clear that if benzene has the three ethylenic linkages as in the Kekulé formula the value of unsaturation would be larger than that in hexatriene. The fact that it is approximately the same must be regarded as accidental and indicating some other structure. We may here observe that both the refractivity and magnetic rotatory power of benzene are less than would be expected from the Kekulé formula; but the parallel between the two is not complete, since the refractive power of benzene is actually below the normal calculated for three "isolated" ethylene linkages, whilst with magnetic rotation this is certainly not the case.

In dealing with the derivatives of benzene we may first consider substances containing an unsaturated side-chain attached to the nucleus. We here find that when the ethylenic carbon atom is directly united to the nucleus the value of unsaturation is very much larger than that observed in the simple unsaturated olefines; but when a screen of saturated groups is placed between the ethylenic and benzene systems the unsaturated value of the former approximates to the normal. The following substances afford illustration of these relations.

TABLE XIV.

ETHYLENE LINKAGE CONJUGATED WITH BENZENE NUCLEUS.

Substance.	Formula.	$M_{\mu e}$	Difference for un-saturation.
Styrol	$C_6H_5CH=CH_2$	16·041	2·627
Ethyl benzene . . .	$C_6H_5CH_2$—CH_3. . . .	13·414	
Propenyl benzene . .	$C_6H_5CH=CH . CH_3$ . .	17·599	3·046
Propyl benzene . .	$C_6H_5CH_2CH_2CH_3$ . .	14·553	
Isobutenyl benzene .	$C_6H_5CH=C(CH_3)_2$ . .	18·362	2·747
Isobutyl benzene . .	$C_6H_5CH_2—CH(CH_3)_2$ . .	15·615	
Ethyl cinnamate . .	$C_6H_5CH=CHCOOEt$.	20·006	3·837
Ethyl hydrocinnamate	$C_6H_5CH_2CH_2COOEt$ . .	16·169	
Indene	C_6H_4 ⟨CH=CH / CH_2⟩	16·202	2·274
Hydrindene . . .	C_6H_4 ⟨CH_2 / CH_2 / CH_2⟩	13·928	
Stilbene	$C_6H_5CH=CHC_6H_5$ . .	33·143	8·166 [1]
Dibenzyl	$C_6H_5CH_2—CH_2C_6H_5$ . .	24·977	

ETHYLENIC LINKAGE SCREENED FROM BENZENE NUCLEUS.

Allyl benzoate . .	$C_6H_5CO . OCH_2CH=CH_2$	15·722	0·849
Propyl benzoate . .	$C_6H_5CO . OCH_2CH_2CH_3$.	14·873	
Phenyl allyl ether. .	$C_6H_5OCH_2CH=CH_2$ . .	17·134	0·947
Phenyl propyl ether .	$C_6H_5OCH_2CH_2CH_3$ . .	16·187	

[1] It should be noted that with some of the unsaturated substances in this table part of the exalted value for unsaturation may be due to the fumaroid condition which has the anomaly of about + 0·5 units; but this does not affect the conclusions.

Moreover, the comparison between isoeugenol and eugenol is worthy of mention; in isoeugenol, which contains the ethylenic carbon contiguous to the benzene nucleus, the rotatory power is greater than with the non-conjugated isomeride.

CH=CH—CH₃

CH₂—CH=CH₂

Isoeugenol.

Eugenol.

$M_{16}^{\circ} = 21\cdot469.$
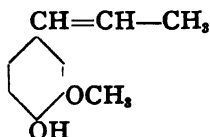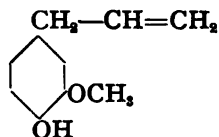
$M_{16}^{\circ} = 18\cdot727.$

Turning to other derivatives of benzene we are met by the difficulty that it is impossible to obtain for comparison with the experimental rotations the normal values which are free from the effect of conjugation. The most that can be done is to study the disturbance produced by substitution on the anomaly of the benzene nucleus. In the comparisons which will be subsequently made, the "calculated" values are obtained by adding the rotatory effect of the substituent as found in fatty compounds to the rotation of the benzene nucleus; and in a few cases the calculation is shown in detail.

We may divide substituents into two classes : those which increase the anomaly of the nucleus and those which decrease it. As examples of the former type of substituent we have the highly unsaturated groups, NH_2, $NHCH_3$, $N(CH_3)_2$, C_6H_5, OCH_3, and the previously mentioned ethylenic linkage. Thus—

Aniline, $C_6H_5NH_2$ (obs.) . . . . . M = 16·076

„   (calc.). . . . . M = 12·25

Disturbance . . . . . = +3·82

Diphenyl, $(C_6H_5)_2$ (obs.) . . . . . M = 25·304

„ $2(C_6H_5—H)$ [1] (calc.) . . . M = 22·06

Disturbance . . . . . = +3·24

[1] See Table on p. 483.

Dimethyl aniline, $C_6H_5N(CH_3)_2$ (obs.)   M =   22·88

    ,, $C_6H_6 + N + 2C + 5H^1$ (calc.) M =   14·30

Disturbance . . . . . = +8·58

Phenetole, $C_6H_5OC_2H_5$ (obs.) . . .   M =   15·129

    ,, $C_6H_6 + O + 2C + 4H^1$ (calc.) .   M =   13·524

Disturbance . . . . . = +1·60

When more than one of these groups is present, the conjugation is multiplied, and consequently the anomaly becomes larger than in the singly substituted compounds. For example—

Substance.	$M_{15°}$ (obs.).	M′ (calc.).	Difference.
o. Phenylene diamine . . .	19·391	13·22	+ 6·17
m. Phenylene diamine . . .	18·843	13·22	+ 5·62
Dimethyl *p*. phenylene diamine	26·239	15·27	+10·97
Hydroquinone dimethyl ether.	16·717	13·71	+ 3·00

On the other hand, the anomaly is reduced by partially saturating the substituent or by isolating it from the benzene nucleus with a saturated group. To illustrate the effect of saturation we may compare the amino compounds with their hydrochlorides and acetyl derivatives.

TABLE XV.

Substance.	$M_{15°}$	Disturbance in rotation of nucleus.
Aniline	16·076	+3·82
Acetanilide	16·003	+1·95
Aniline hydrochloride. . . .	16·394	+1·9
Dimethyl *p*. toluidine	22·842	+7·52
Dimethyl *p*. toluidine hydrochloride	18·465	+0·90
Dimethylaniline	22·888	+8·58
Dimethylaniline hydrochloride .	18·326	+1·78
o. Phenylene diamine	19·391	+6·17
o. Phenylene diamine hydrochloride	21·329	+3·52

[1] See Table on p. 483.

Among the groups which decrease the anomaly of the benzene nucleus we have chlorine, the nitro, carbethoxyl, nitrile and methyl groups. From the relation between

$$\text{Nitropropane} \quad . \quad . \quad . \quad M = 3\cdot819$$
$$\text{Propane} . \quad . \quad . \quad M \text{ (calc.)} = 3\cdot590$$

it follows that H displaced by NO_2 in fatty series $= +0\cdot229$. Thus—

$$\text{Nitrobenzene} \quad . \quad M \text{ (calc.)} \; 11\cdot284 + 0\cdot229 = 11\cdot51$$
$$\text{whereas } M \text{ (obs.)} = \quad 9\cdot36$$
$$\text{hence disturbance} = -2\cdot15$$

Comparing hydrocarbons with the esters of fatty acids—

$$\text{Ethyl capronate} . \quad . \quad . \quad . \quad M = 8\cdot509$$
$$\text{Pentane} \quad . \quad . \quad . \quad . \quad . \quad . \quad M = 5\cdot638$$
$$\text{Difference} . \quad . \quad . \quad = 2\cdot871$$

$$\text{Ethyl oenanthylate} \quad . \quad . \quad . \quad M = 9\cdot541$$
$$\text{Hexane} \quad . \quad . \quad . \quad . \quad . \quad . \quad M = 6\cdot670$$
$$\text{Difference} . \quad . \quad . \quad = 2\cdot871$$

$$\text{Ethyl pelargonate} \quad . \quad . \quad . \quad . \quad M = 11\cdot571$$
$$\text{Octane} \quad . \quad . \quad . \quad . \quad . \quad . \quad M = 8\cdot722$$
$$\text{Difference} . \quad . \quad . \quad = 2\cdot849$$

it is seen that the normal value for hydrogen displaced by carbethoxyl is approximately $+2\cdot86$ units of rotation.   Thus for

$$\text{Ethyl benzoate, } C_6H_5COOEt . \quad . \quad . \quad M \text{ calculated} = \quad 14\cdot14$$
$$M \text{ observed} = \quad 13\cdot85$$
$$\text{Disturbance} = -0\cdot29$$

$$\text{Ethyl terephthalate, } C_6H_4(COOEt)_2 . \quad M \text{ calculated} = \quad 17\cdot00$$
$$M \text{ observed} = \quad 16\cdot11$$
$$\text{Disturbance} = -0\cdot89$$

It may be shown by similar methods that the following substances belong to this class :—

TABLE XVI.

Substance.	$M_{15°}$ (obs.).	M (calc.).	Depression.
Chlorobenzene . . .	12·51	12·76	−0·25
p. Dichlorobenzene . .	13·65	14·24	−0·59
Benzonitrile	11·85	12·05	−0·20
Acetophenone . . .	12·597	13·67	−1·07

Some of these compounds show such a small depression that they might be considered as normal; but the effect of substitution becomes clearer when the substituents are multi-plied, as with ethyl terephthalate and *p*. dichlorobenzene. The cumulative effect of weakly active groups can be clearly traced in the aromatic hydrocarbons of which four consecutive members have been examined.

TABLE XVII.

Substance.	$M_{15°}$ (obs.).	M (calc.).	Depression.
Benzene	11·284	—	±0·0
Toluene	12·150	12·30	−0·15
m. Xylene	12·853	13·32	−0·47
Mesitylene	13·366	14·34	−0·98

It is interesting to find that the methyl group, which is usually assumed to be saturated, disturbs the balance of affinities in the benzene system, and it may be recalled that the refractive powers of these hydrocarbons lead to a similar result.

A further point of interest in the action of these groups is that those which depress the anomaly of the nucleus are, with

the exception of methyl, of so-called negative properties, the exaltant dimethylamino and amino groups being of positive character.   Moreover, there seems to be a connection between the conditions which they impart to the benzene nucleus and their directing influence.   The carboxyl, nitro, nitrile, and acetyl groups generally direct an entrant group to the meta position, whilst amino, hydroxyl, and phenyl direct to the ortho and para positions.

When the substituent is screened from the nucleus by an intervening group of more saturated character, such as methylene, it is clear that the mutual influence of the unsaturated group and the nucleus will be lessened, and the benzene system will therefore return to its normal condition.   The best examples of this process are collected in the following table.

TABLE XVIII.

Substance.	Formula.	$M_{16°}$ (obs.).	M (calc.).	Disturbance.
Diphenyl	$C_6H_5—C_6H_5$. . . .	25·304	22·06	+3·24
Diphenyl methane .	$C_6H_5—CH_2—C_6H_5$. .	23·845	23·08	+0·76
Dibenzyl	$C_6H_5.CH_2.CH_2.C_6H_5$	24·977	24·10	+0·87
Ethyl benzoate . .	C_6H_5COOEt . . .	13·854	14·14	−0·29
Ethyl phenylacetate .	$C_6H_5CH_2COOEt$ . .	14·982	15·16	−0·18
Ethyl hydrocinnamate	$C_6H_5CH_2CH_2COOEt$.	16·169	16·18	−0·01
Aniline	$C_6H_5NH_2$	16·076	12·25	+3·82
Benzylamine . . .	$C_6H_5CH_2NH_2$ . . .	13·646	13·27	+0·37
Anisole	$C_6H_5OCH_3$	13·958	12·40	+1·55
Methyl benzyl ether .	$C_6H_5CH_2OCH_3$. . .	13·417	13·42	±0·0

In concluding the study of aromatic compounds it may be observed that the rotations of ortho, meta, and para isomers are not identical.   From the few instances studied it seems that the ortho derivative has the greatest rotation, but the meta and para follow in varying order.

To illustrate the magnitude of the difference between these isomerides we may employ the following substances :—

TABLE XIX.

Substance.	$M_{18°}$	Substance.	$M_{18°}$
o. Cresol . . .	13·382	*o*. Xylene . . .	13·345
m. Cresol . . .	12·869	*m*. Xylene . .	12·810
p. Cresol . . .	12·776	*p*. Xylene . . .	12·859
Ethyl phthalate .	16·909	*o*. Toluidine . .	17·200
Ethyl isophthalate	16·928	*m*. Toluidine . .	16·210
Ethyl terephthalate	16·117	*p*. Toluidine . .	16·188

§ 10. *INORGANIC COMPOUNDS*[1]

The magnetic rotatory power of salt solutions has been very thoroughly studied with a view to establishing relations between this property and ionization. The earliest observations were made with hydrochloric and hydrobromic acids by Perkin, who showed that the rotations of these acids in non-ionizing media such as amyl ether, are equal to the sum of the ordinary rotatory effects of hydrogen and halogen, whereas in water they have a different rotatory power which, on diluting the solution, changes continuously until a constant value is reached. Ostwald then pointed out that this behaviour is in accord with the ionic theory, and he confidently hoped that future research would add further support to this evidence. However, later experiments have shown that the question of the effect of solution on the magnetic rotation of a salt is very complex, and at present it is imperfectly understood. Electrolytes vary in the response they show to dilution. Some, indeed, like the halogen acids, behave in accordance with the ionic theory. In concentrated aqueous solution and in non-ionizing media their rotatory power approximates to the normal, and dilution of the aqueous solutions causes the

[1] Ostwald, *Trans. Chem. Soc.*, **59**, 198 (1891) ; Perkin, *Trans. Chem. Soc.*, **55**, 680 (1889) ; **65**, 20 (1894) ; **63**, 57 (1893) ; *Proc. Chem. Soc.*, 140, (1890) ; Jahn, *Wied. Ann.*, **43**, 280 (1891) ; Wachsmuth, *Wied. Ann.*, **44**, 380 (1891) ; Schönrock, *Zeit. Phys. Chem.*, **11**, 753 (1893) ; **16**, 29 (1895) ; Humburg, *Zeit. Phys. Chem.*, **12**, 401 (1893) ; Oppenheimer, *Zeit. Phys. Chem.*, **27**, 447 (1898) ; Forchheimer, *Zeit. Phys. Chem.*, **34**, 19 (1900).

rotation to increase to a constant value. On the other hand, there are numerous substances whose rotations decrease with increasing ionization, and yet others which remain practically unaffected by change in concentration. From the lack of any theory connecting these facts we must be content with merely examining a few examples of each type of electrolyte.

TABLE XX.

CASES IN WHICH ROTATION INCREASES WITH DILUTION.

Substance.	Per cent. in solution.	M.	Substance.	Per cent. in solution	M.
HCl in amyl alcohol	6·8	4·02	LiCl in water . .	42·3	4·17
,, in ethyl alcohol	9·7	4·2	,, ,, . .	24·1	4·56
,, ,,	6·6	4·49	,, ,, . .	16·7	4·68
,, in water . .	41·7	4·04	Li₂SO₄ in water .	23·48	2·38
,, ,, . .	36·5	4·22	,, ,, .	16·41	2·64
,, ,, . .	30·8	4·30	,, ,, .	7·71	3·11
,, ,, . .	25·6	4·40	NH₄I in water . .	60·4	19·93
,, ,, . .	15·6	4·42	,, ,, . .	30·5	20·05
,, ,, . .	11·4	4·77	,, in alcohol .	21·1	18·95

CASES IN WHICH ROTATION DECREASES WITH DILUTION.

Na₂SO₄ in water. . .	26·38	2·95	LiNO₃ in water. . .	56·56	1·12
,, ,, . .	16·0	2·88	,, ,, . .	26·16	0·98
,, ,, . .	12·21	1·21	,, ,, . .	18·17	0·93
H₂SO₄ in water . . .	99·8	2·30	HNO₃ in water. . .	99·4	1·21
,, ,, . .	73·0	2·11	,, ,, . .	56·4	0·98
,, ,, . .	35·1	1·95	,, ,, . .	32·3	0·85
,, ,, . .	18·9	1·92	,, ,, . .	26·8	0·80

CASES WHERE ROTATION REMAINS ALMOST CONSTANT.

Acetic acid . . .	100·0	2·47	(NH₄)₂SO₄ in water	40·28	4·98
,, in water .	39·0	2·46	,, ,,	6·67	5·01
,, ,, .	12·7	2·40	MgSO₄ in water .	25·46	2·03
,, ,, .	9·7	2·49	,, ,,	10·14	2·04
,, in benzene	31·3	2·52	CdBr₂ in water . .	46·57	40·18
,, ,, .	10·8	2·47	,, ,, .	12·46	40·18
,, in toluene	38·4	2·43	CdI₂ in water . .	44·53	43·68
,, ,, .	9·6	2·45	,, ,, .	7·26	42·37
NaCl in water . .	3·97 (normal)	1·64	KCl in water . .	37·4 (normal)	1·32
,, ,, . .	2·01	1·67	,, ,, . .	18·7	1·34
,, ,, . .	0·97	1·66	,, ,, . .	0·93	1·31

Also the rotations of the aqueous solutions of ammonium and sodium salts of formic and acetic acids are unaffected by dilution.

TABLE XXI.

Molecular composition of solution.	M.	Molecular composition of solution.	M.
$HCOONH_4 + 3H_2O$ . .	3·363	$CH_3COONH_4 + 4·75H_2O$	4·246
$HCOONH_4 + 10·4H_2O$.	3·333	$CH_3COONH_4 + 13·13H_2O$	4·247
$HCOONa + 5·4H_2O$ . .	2·364	$HCOONa + 12·54H_2O$.	2·331

It should be noticed that the molecular rotations of these salts are approximately equal to the sum of the rotations of their constituents. Thus we have

NH_3 . . . M = 1·818 NH_3 . . . . M = 1·818
$HCOOH$ . . M = 1·671 CH_3COOH . M = 2·525

$HCOONH_4$. M = 3·489 CH_3COONH_4 . M = 4·343

   observed . M = 3·363   observed . M = 4·247

In both these examples the calculated values slightly exceed those found in experiment, and it should be noted that Perkin has claimed that this is a general rule applying to the formation of salts. We see, then, that the relations between ionization and magnetic rotation are not clearly defined, and at present just sufficient data have been collected to render further research on the question both interesting and desirable. Attention may here be drawn to the similarity between the refractive and magnetic rotatory powers of salt solutions in their behaviour on dilution.

The additive nature [1] of the rotatory power of salt solutions, to which allusion has been made in the formates and acetates, is further illustrated by the relations between inorganic salts

[1] See Jahn, *Wied. Ann.*, **43**, 280 (1891); and for other examples Schönrock, *Lehrbuch der Chemie;* Graham Otto, I. **3**, 806; Braunschweig, 1898.

containing the same anion. The following table shows the molecular rotatory power (M) of a few salts in aqueous solution.

TABLE XXII.

Substance.	M.	Substance.	M.
HCl	4·67	NaBr . . .	9·19
LiCl	4·61	KBr. . . .	9·36
NaCl. . . .	5·36	CaBr$_2$ . . .	2 × 8·80
KCl	5·66	SrBr$_2$ . . .	2 × 9·08
CaCl$_2$ . . .	2 × 4·69	BaBr$_2$ . . .	2 × 9·27
SrCl$_2$ . . .	2 × 4·85	CdBr$_2$ . . .	2 × 9·85
BaCl$_2$ . . .	2 × 5·04		
CdCl$_2$ . . .	2 × 5·89	Li$_2$SO$_4$ . . .	2·27
		Na$_2$SO$_4$ . .	3·54
NaI	18·46	K$_2$SO$_4$ . . .	3·57
KI	18·95	CdSO$_4$ . . .	5·17
CdI$_2$	2 × 20·4		

It will be seen that equivalent amounts of salts with the same anion have approximately equal rotations. Moreover, if the rotations of corresponding members in two series are compared, it is found that there is a nearly constant difference between the two series taken member by member. Thus between bromides and chlorides—

$$NaBr - NaCl = 3·83$$
$$KBr - KCl = 3·70$$
$$\tfrac{1}{2}CaBr_2 - \tfrac{1}{2}CaCl_2 = 4·10$$
$$\tfrac{1}{2}SrBr_2 - \tfrac{1}{2}SrCl_2 = 4·22$$
$$\tfrac{1}{2}BaBr_2 - \tfrac{1}{2}BaCl_2 = 3·80$$

and between iodides and chlorides

$$NaI - NaCl = 13·10$$
$$KI - KCl = 13·29$$
$$\tfrac{1}{2}CdI_2 - \tfrac{1}{2}CdCl_2 = 14·55$$

and so on. In this way it is possible to obtain values for the displacement of the anions just as can be done with groups

in organic compounds; and from the data which have been quoted it may be calculated that—

Replacement of Br by Cl = $-4\cdot0$
and of I by Cl = $-13\cdot5$ approximately

It is scarcely to be expected that the differences between the series should be more constant since the effect of solution, which varies in sign and magnitude from salt to salt, is neglected.

For the present it must remain doubtful whether similar relations exist between salts containing a common anion, since the replacement-values of the metals, *e.g.*—

$$NaCl - KCl = -0\cdot30 \qquad NaI - KI = -0\cdot49$$
$$NaBr - KBr = -0\cdot25 \qquad Na_2SO_4 - K_2SO_4 = -0\cdot03$$

are small and the variations relatively large. However, from the relations already noted between salts containing a common cation it seems probable that further research will show that the rotation of a salt may be approximately equal to the sum of the effects of the anion and cation; but this cannot be accurately demonstrated until some means are found of eliminating the effect of the dissolved state and dilution. As bearing on this question we may again refer to the work of Perkin on the ammonium and sodium salts of formic and acetic acids, and to the rotation of ammonium nitrate. Perkin found that the rotatory power of the latter substance is approximately equal to the sum of the rotations of ammonia and nitric acid, whereas the ammonium salts of the halogen acids are abnormally high. He therefore assumed that the nitrates of the metals are normal, and, making use of the values found for their aqueous solutions, he thence calculated the values of the metals themselves. The numbers resulting from this process are shown in Table XXIII.

The atomic rotations of these and other elements have been independently calculated by Schönrock, but in a rather more complicated manner. The results clearly show that the atomic rotatory equivalents are connected with the positions

TABLE XXIII.

Nitrate of	M.	Value of metal.
Sodium . . .	1·284	0·558
Potassium . . .	1·535	0·809
Lithium . . .	1·124	0·398
Calcium . . .	2·143	0·691
Magnesium . .	2·029	0·577

of the elements in the periodic system. For the actual data the reader must be referred to the original literature.

Having now considered the chief relations between magnetic rotation and chemical constitution, we may turn to the application of this property in chemical problems.

§ II. *APPLICATION OF MAGNETIC ROTATION*

The Nature of Unstable Compounds.—In many instances it is possible to isolate from a mixture of two substances a definite compound which is composed of these in molecular proportions; but it is often doubtful whether the new substance is formed by rearrangement of the atomic affinities of the components, or whether it results from mere molecular combination. It is evident that a substance formed by molecular combination will possess a rotatory power equal to the sum of the rotations of the constituents; but if atomic combination takes place the molecular rotation will have another value. These considerations furnish a method of distinguishing the two modes of combination. Oppenheimer[1] has shown that the molecular rotations of the halides of cadmium in aqueous solution remain approximately constant at all dilution, and, since it is known from the cryoscopic and other methods that concentrated solutions of these salts contain molecular aggregates, it may be concluded that rotatory power is unaffected by molecular aggregation in solution. The behaviour of these complex cadmium salts may be contrasted with that

[1] Oppenheimer, *Zeit. Phys. Chem.*, **27**, 447 (1898).

of the double salts formed by the halides of mercury. Schönrock,[1] who investigated these substances, first showed that salts possessing the same negative ion, as a rule, do not exert any mutual influence so far as their rotations are concerned when present in the same solution. Thus the rotations calculated for the mixed solutions from the sum of the rotatory effects of the salts present agree well with those found in experiment, *e.g.*—

Salts in solution.	Rotation.	
	Found.	Calculated.
Na_2SO_4, $MgSO_4$ . .	0·358–0·376	0·378
Na_2SO_4, $CdSO_4$ . .	0·388–0·499	0·403
Na_2SO_4, $MnSO_4$ . .	0·407–0·371	0·388

But aqueous solutions of mercuric chloride with sodium chloride and mercuric iodide with potassium iodide give abnormal values—

Composition of solution.	Molecular rotation.	
	Found.	Calculated.
NaCl, $HgCl_2$ . . .	23·757	18·953
2KI, HgI_2. . . .	135·557	84·073

The large increase in rotatory power produced by mixing the salts shows that some redistribution of the atomic affinities has occurred, and it is scarcely necessary to remark that chemical evidence supports this conclusion.

Perkin has investigated the aqueous solutions of some compounds which may be suspected of combining with that solvent. Thus chloral,[2] CCl_3CHO, has the molecular rotation 6·591, so that chloral hydrate, $CCl_3CHO . H_2O$, if a molecular compound, should have $M = 6·591 + 1 = 7·591$. Experiment

[1] Schönrock, *Zeit. Phys. Chem.*, 17, 753 (1895).
[2] Perkin, *Trans. Chem. Soc.*, 51, 808 (1887).

shows that chloral hydrate has the molecular rotation 7·037, whence it may be inferred that the constitution of chloral is changed by the addition of the molecule of water, and chloral hydrate should be represented as $CCl_3CH(OH)_2$.' Similarly it is found that acetic aldehyde in aqueous solution at the ordinary temperature has a slightly greater rotatory power than in the anhydrous state, thus indication is given of the existence of the aldehydrol $CH_3CH(OH)_2$. It may be noted that Colles[1] recently has isolated this compound at low temperatures.   On the other hand, Perkin has shown [2] that the constant boiling mixture of formic acid and water of the composition $4CH_2O_2 . 3H_2O$ is a molecular compound.

Tautomeric Compounds.[3]—From the organic chemist's standpoint the utility of magnetic rotation is perhaps seen to its best advantage in the study of tautomeric compounds.   The method of investigation is very simple, since all that is required is to compare the values calculated for either tautomeric form with that found in experiment under given conditions.   In most cases Perkin, to whom all the experiments on this subject are due, was able to obtain decisive evidence of the ketonic or enolic structure.   We may at once proceed to consider the more important results.

Ethyl acetoacetate $CH_3COCH_2COOC_2H_5$

The rotation of the enolic form of this ester may be calculated as follows :—

<div align="center">

I.

Ethyl lactate	5·720
CH_2	1·023
Ethyl hydroxybutyrate	6·743
Unsaturation	+1·112
$CH_3C(OH)=CH . COOC_2H_5$ . .	7·855

</div>

[1] *Trans. Chem. Soc.*, **89**, 1246 (1908).
[2] Perkin, *Trans. Chem. Soc.*, **49**, 777 (1886).
[3] Perkin, *Trans. Chem. Soc.*, **61**, 800 (1892) ; **65**, 815 (1894).

II.

Ethyl crotonate . . . . 7·589
H˙by OH, as in alcohols . . . .+0·194
_____
7·783

And we have seen that according to theory the rotation of the ketonic form is 6·529. Since experiment gave—

at 16·2° M = 6·501
at 90·5° M = 6·470

it is clear that the sample of acetoacetic ester examined was the pure ketonic compound; moreover, on heating the substance no change in constitution occurs, for the slight decrease is of the same order as that found with simple fatty esters. It has been further shown that the mono and dialkyl derivatives are ketonic; indeed, this might be anticipated from the previous result with the parent substance. The experimental data from this group are collected in the following list.

TABLE XXIV.

Substance.	Formula.	Theory.		Found.
		Enolic.	Ke-tonic.	
Ethyl acetoacetate . . .	CH_3COCH_2COOEt . .	7·8	6·529	6·501
Ethyl ethyl acetoacetate[1] .	$CH_3COCH(C_2H_5)COOEt$	—	8·36	8·329
Ethyl di-ethyl acetoacetate[1] .	$CH_3COC(C_2H_5)_2COOEt$.	—	10·28	10·115
Ethyl di-methyl acetoacetate[1]	$CH_3COC(CH_3)_2COOEt$.	—	8·35	8·169
Methyl di-methyl acetoacetate[1]	$CH_3COC(CH_3)_2COOMe$.	—	7·26	7·13

[1] The calculated values of these compounds are obtained from that of acetoacetic ester with the aid of the following :—

Ethyl ester of malonic acid . . . . . . 7·410
,, ,, ethyl malonic acid . . . . 9·272
,, ,, diethyl malonic acid . . . 11·197
,, ,, dimethyl malonic acid . . . 9·268

The adjacent homologues of acetoacetic acid, pyruvic and levulinic acids, have the ketonic structure. Thus—

.

Pyruvic acid $CH_3COCOOH$

Series const. formic acid	.	.	.	.	0·648
. " ketones	.	.	.	.	0·375
				2)$\overline{1·023}$
Series const. pyruvic acid	.	.	.	.	0·511
Add 3 × CH_2	.	.	.	.	3·069

Calculated for pyruvic acid . . 3·580

Whereas experiment gave 3·567

Levulinic acid $CH_3COCH_2CH_2COOH$

Ketonic form . . . . 5·60–5·50 ⎫
Enolic form . . . . 6·89–6·83 ⎬ calculated [1]

Experiment gave 5·509

As further examples of substances allied to acetoacetic acid, we may take acetone-dicarboxylic ester and benzoyl-acetic ester.

Acetone-dicarboxylic ester $COOEt . CH_2COCH_2COOEt$

The rotation of the ketonic form may be calculated as follows—

I.

Ethyl acetoacetate . . . . 6·501
H by —COOEt . . . . 2·86

Calculated . . . . M = 9·36

[1] See p. 481.

II.

Series const. ester of dibasic acid . . . 0·140
Series const. ketones . . . . 0·375

∴ series const. acetone dicarboxylic ester   0·257
    Add 9CH$_2$. . . . . 9·207

    Calculated. . . . . . . M = 9·464

The average calculated value is about 9·41

The data of experiment—

$$M = 9·604 \text{ at } 16·5°$$
$$M = 9·374 \text{ at } 94°$$

show that at ordinary temperatures the enolic form of the ester is present in small quantity; but this, on being heated, is apparently transformed to the ketonic isomeride, since the fall in rotation on raising the temperature to 94° is larger than that usually found in aliphatic compounds.

With benzoyl acetic ester there is some difficulty in obtaining theoretical values upon which reliance may be placed. However, the rotation of the ketonic ester may be approximately calculated as follows—

Ethyl benzoylacetate $C_6H_5COCH_2COOEt$

Ethyl benzene, $C_6H_5CH_2CH_3$ . . . . $M_{18°} =$ 13·382
Aceto phenone, $C_6H_5COCH_3$ . . . . $M_{18} =$ 12·597

Hence CH$_2$ by CO =   −0·785

Ethyl hydrocinnamate, $C_6H_5CH_2CH_2COOEt$ $M_{18} =$ 16·169
Ethyl benzoylacetate, $C_6H_5COCH_2COOEt$ M   =   15·384

Since the sample of the ester examined gave M = 16·393 at 18·8°, we may conclude that it contained the enolic ester—
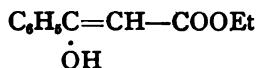
$$C_6H_5C{=}CH{-}COOEt$$
$$\overset{.}{O}H$$

It is difficult to estimate the rotation of the latter isomeride with any approach to accuracy, but since ethyl cinnamate $C_6H_5CH=CHCOOEt$ has $M_{18°} = 20·006$, it is clear that the specimen of benzoylacetic ester did not entirely consist of the enolic isomeride. On turning to the more complicated ketones, mono and diacetyl acetone, we again meet with the difficulty of calculating reliable values for the unsaturated isomerides. In acetyl acetone we may have—

The diketo form, $CH_3COCH_2COCH_3$

The keto-enol form, $CH_3CO—CH=C.CH_3$
$\overset{\textstyle .}{O}H$

The di-enol form, $CH_3C=C=C—CH_3$
$\quad\overset{\textstyle .}{O}H\quad\overset{\textstyle .}{O}H$

or $CH_2=C—CH=C—CH_3$
$\quad\overset{\textstyle .}{O}H\qquad\overset{\textstyle .}{O}H$
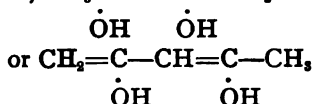
The rotation of the diketonic form may be calculated as follows :—

$$CH_3COCH_2COCH_3$$

I.

Acetoacetic ester . . . . $M = 6·501$

Ethyl acetate . . . . . $M = 4·462$

Hence H by $CH_3CO—$ . . $= +2·039$

And since acetone . . . $M = 3·514$

$\therefore CH_3COCH_2COCH_3$ . . $M = 5·553$

II.

Series const. (acetone) . . . $= 0·445$

$5CH_2$ . . . . $= 5·115$

$\therefore CH_3COCH_2COCH_3$ . . . $= 5·560$

In the keto-enolic structure the value of the conjugated unsaturation

$$-CH=CH-\underset{\underset{\textstyle O}{\|}}{C}-$$
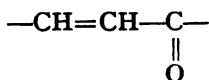
is uncertain; but assuming this to be the same as in the $\alpha-\beta$ unsaturated acids we may proceed thus—
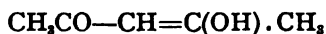
$$CH_3CO—CH=C(OH).CH_3$$

I.

Aceto-propyl alcohol . . . . $M = 5\cdot544$
Difference between 1^{ry} and 2^{ndary} propyl alcohol $= 0\cdot251$
Unsaturation . . . . $= 1\cdot112$
_____
$CH_3CO.CH=C(OH).CH_3$ . . . . . . $= 6\cdot907$

II.

Series const. isopropyl alcohol . . . . . . $= 0\cdot950$
      „   ketones . . . . $= 0\cdot375$

Hence series const. keto-enolic form . . . . $= 0\cdot662$
$5CH_2$ . . . . $= 5\cdot115$
Unsaturation. . . . . $= 1\cdot112$
_____
$\therefore CH_3COCH=C(OH).CH_3$ . . . . . . $= 6\cdot889$

In the absence of any reliable data concerning the value of the structures $=C=$ or $>C=CH—CH=C<$, the rotations of the di-enolic compound must remain uncertain; but it may be observed that Perkin has calculated it in the following manner :—

$$CH_3C(OH)=C=C(OH).CH_3$$

I.

Glycol . . . . $M = 2\cdot943$
$3CH_2$. . . . . $M = 3\cdot069$
Unsaturation $\times 2$ . . . . $M = 2\cdot224$
_____
$CH_3C(OH)=C=C(OH)CH_3$. . . . . $= 8\cdot236$

II.

Keto-enolic form . . . . M = 6·889
Diketonic form . . . . M = 5·553

Change of ketonic to enolic structure . . = 1·336

Hence $CH_3C(OH)=C=C(OH).CH_3$. = 8·225

The experimental and theoretical rotations of acetyl acetone and its alkyl derivatives are collected in the following table.

TABLE XXV.

Substance.	M (calc.).			M (obs.).	Tempera-ture.
	Diketo.	Keto-enol.	Dienol.		
Acetylacetone . . .	5·553	6·889	8·236	7·166 6·599	16·6° 93·0
Methyl acetylacetone .	6·519	7·859	9·295	7·237 6·670	16·3 96·4
Ethyl acetylacetone . .	7·534	8·882	10·218	7·890 7·562	18·8 92·9
Dimethyl acetylacetone .	7·599	—	—	7·046 6·995	20 92

On examining these data it is seen that acetylacetone and its mono-alkyl derivatives possess greater rotatory powers than that expected for the ketonic form, and we must conclude that these ketones are to a certain extent enolized. It is further evident that insertion of the alkyl group depresses the tendency to enolize, and the same effect is observed on raising the temperature; so that in the monoethyl derivative at 90° the united efforts of those influences cause the enolic structure almost to vanish. Dimethyl acetylacetone, even at the ordinary temperature, is completely ketonic. The restraining influence of the alkyl group on enolization is further seen in

the rate of change of the ketonic to enolic structure when the heated substance is cooled. A sample of acetylacetone which has been heated to 93° and then cooled regains the original high rotation in two or three hours; but the methyl derivative, when treated in the same manner, does not resume the initial rotation until three weeks have elapsed. From the data quoted in the previous table Perkin calculated the percentage of each type of isomeride present in the substances examined. The results are untrustworthy on account of the necessary assumption that not more than two kinds of isomeride are present, and because of the uncertainty in the theoretical values, but they may be here reproduced since they clearly demonstrate the ketonizing effect of substitution.

TABLE XXVI.

Substance.	Percentage of—		
	Diketo.	Keto-enol.	Dienol.
Acetyl acetone	—	80·0	20
Methyl acetylacetone . . .	46·4	53·6	—
Ethyl acetylacetone . . .	74·0	26·0	—

The theoretical values of four of the possible forms of diacetyl acetone are as follows—

$CH_3COCH_2COCH_2COCH_3$ . . . . 7·606
$CH_3C(OH)=CHCOCH_2COCH_3$ . . . . 8·842
$CH_3C(OH)=CH—COCH=C(OH)CH_3$ . . . . 10·158
$CH_3C(OH)=C=C(OH)—CH=C(OH).CH_3$ . . 11·540

whilst experiment gave

$$M = 10·223 \text{ at } 60·4°, \text{ and } 9·587 \text{ at } 96·3°$$

From the large decrease in rotation (0·636) caused by a rise of thirty degrees, it is evident that at ordinary temperatures this substance contains the hydroxylic isomerides.

The influence of various solvents on the rotatory power of

tautomeric substances has not been thoroughly studied. Perkin suggested this inquiry but did not pursue it far; he found that acetyl acetone is less enolized in acetic anhydride solution than when undissolved.

The Configuration of Ethylenic Compounds.—There are a few instances in which magnetic rotation may be applied to determine the configuration of an ethylenic compound of the type $XCH=CHY$. Here use is made of the previously observed fact that the rotation of the fumaroid isomer

$$CH—X$$
$$\parallel$$
$$Y—CH$$
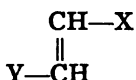
is abnormally high, whilst that of the maleinoid form is normal. The following cases will serve to illustrate this application.

Ethyl crotonate $CH_3CH=CHCOOEt$

The rotation of this substance compared with that of ethyl butyrate—

$$CH_3CH=CHCOOEt \quad M = 7\cdot589$$
$$CH_3CH_2CH_2COOEt \quad M = 6\cdot477 \Big\} \text{Diffce. } 1\cdot112$$
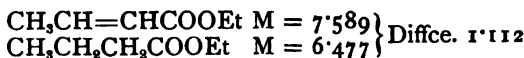
shows the effect of unsaturation to be normal, hence the configuration would be analogous to that of maleic acid

$$HC—CH_3$$
$$\parallel$$
$$HC—COOEt$$
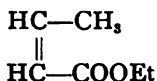
in confirmation of the chemical evidence.[1]

Ethyl β-ethoxy crotonate $CH_3C(OEt)=CHCOOEt$

A similar comparison made in this case

$$CH_3C(OEt)=CHCOOEt \quad M = 10\cdot430$$
$$CH_3CH(OEt)CH_2COOEt \quad M = 8\cdot687 \Big\} 1\cdot752$$

[1] Wislicenus, *Ann.*, **248**, 281 (1888).

shows that the configuration is fumaroid

$$CH_3—CO—Et$$
$$\|$$
$$HC—COOEt$$
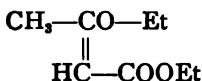
Finally, the contrast between the rotations of the methyl esters of a and β o. methoxyphenyl-acrylic acid

$$a = 21\cdot891$$
$$\beta = 22\cdot359$$

shows that their configurations respectively are—

$MeOC_6H_4CH$	HCC_6H_4OMe
$\|$	$\|$
$MeOOC . CH$	$MeOOC \cdot CH$
a. Ester.	*β*. Ester.

It may be noted that Perkin has employed[1] magnetic rotatory power to determine the structural changes which take place in the *mutarotation* of some of the sugars; but the difficulty in obtaining reliable values for the different structural forms renders the conclusions somewhat untrustworthy.

In conclusion, it may be observed that the application of magnetic rotation to organic chemistry is limited by the many errors which must be committed in obtaining theoretical values with a property of such highly constitutive nature. To eliminate these, much further study of the influence of constitution is required; but, unfortunately, no adequate successor to Perkin has yet taken up this work.

[1] *Trans. Chem. Soc.*, **81**, 177 (1902).

ELECTRICAL PROPERTY

CHAPTER XIV

ANOMALOUS ELECTRIC ABSORPTION

§ I. *NORMAL ELECTRIC ABSORPTION*

WE have seen, when discussing fluorescence and colour, that many substances are capable of absorbing the rapid ether vibrations of light; it is, therefore, interesting to find that matter can absorb also the energy of vibrations of much greater wave length, such as those produced by an oscillating electric discharge. Both conductors and non-conductors may absorb these electric waves. With conductors the absorption is of normal character, and it may be theoretically explained; but with non-conductors the absorption is abnormal. It is with this latter kind of absorption that the influence of chemical constitution has been detected. Before approaching this question we must briefly consider the characteristics of the normal type.

According to the electromagnetic theory of light we have, for insulators, the relation

$$E = n^2 \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

where E represents the dielectric constant of the medium and *n* the electric index of refraction for waves of infinite length. In the experimental determination of dielectric constant either E may be directly measured in a stationary electric field—*i.e.* with waves of infinite length,—or *n* may be found for waves of a given finite length. Although according to theory the foregoing relation (i) holds only for the refractive index of the

medium with infinite waves, practice has shown that approximately the same values of n^2 are obtained with waves of moderate length. Thus Drude,[1] employing waves about one metre long, found for water $n^2 = 80\cdot6$, whilst Nernst[2] and Heerwagen[3] measured E directly by other methods and found $n^2 = 80\cdot5$.

Turning from insulators to bodies of moderate conductivity we find, on measuring the index of refraction for finite electric waves, that satisfactory values for E are no longer obtained. On account of the absorption exerted by the medium, n^2 is always greater than E and the relation becomes— [4]

$$E = n^2(1 - x^2) . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

where x is the absorption-index, a quantity which depends on the decrease in amplitude of the wave on entering the medium.[5] From the study of aqueous solutions of electrolytes Drude[6] has shown that the index of absorption may be calculated from the relation—

$$x = \frac{2s}{1 + \sqrt{1 + 4s^2}} . \quad . \quad . \quad . \quad \text{(iii)}$$

where s is an abbreviation for $\dfrac{c\sigma\lambda}{\epsilon}$, in which $c =$ velocity of light, $\lambda =$ wave length of the electric vibration, $\sigma =$ conductivity of the solution in absolute units, and $\epsilon =$ dielectric constant of water. We see, then, that this absorption can be theoretically calculated from the conductivity of the medium and the wave length of the electric vibration ; it is therefore called normal absorption.

Before proceeding to anomalous absorption we may briefly notice the characteristic behaviour of this normal type with

[1] *Wied. Ann.*, **59**, 17 (1896).

[2] *Zeit. Phys. Chem.*, **14**, 622 (1894).

[3] *Wied. Ann.*, **43**, 35 (1891).

[4] Drude, *Zeit. Phys. Chem.*, **23**, 280 (1897).

[5] x means that the amplitude of the electric vibration on passing through a wave length has decreased in the ratio $1 : e^{2\pi x}$.

[6] Drude, *loc. cit.*, and *Wied. Ann.*, **60**, 28 (1897).

respect to conductivity and wave length. It is evident that increasing conductivity expands the absorptive power; but this relation holds only within narrow limits of conductivity, for very good conductors are non-absorbent. Further, a decrease in wave length of the incident vibrations will be accompanied by a diminution of absorption. Thus the effect of decreasing wave length opposes that of increasing conductivity, and sometimes may obscure it; a conductor of moderate strength will not absorb if the vibrations are of sufficiently short period. For example, Drude[1] finds that ordinary tap-water shows no absorption with 400×10^6 vibrations per second, and an aqueous solution of copper sulphate only absorbs these vibrations when a concentration of 0.5 per cent. is reached.

§ 2. *ANOMALOUS ABSORPTION*

Organic compounds in general possess a very small conductivity, and therefore, if they obey the laws of normal absorption, they will be non-absorbent with short electric waves (*e.g.* $\lambda = 73$ cms.). The majority behave normally, but a few substances are exceptional, and these, although poor conductors, can absorb rapid vibrations. Such behaviour was first observed by Cole[2] with ethyl alcohol; but Drude[3] independently discovered it shortly afterwards in other substances. Drude found that this unexpected absorption is particularly strong with the alcohols; in fact, amyl alcohol is as good an absorbent as an electrolyte of 20,000 times its conductivity. With abnormal absorbents the n^2 of experiment is always less than the dielectric constant of the medium—

$$E > n^2$$

and the effect of change in vibration period of the incident wave is contrary to that found in "normal" cases, a decrease

[1] *Ber.*, **30**, 940 (1897).
[2] *Wied. Ann.*, **57**, 290 (1896).
[3] *Wied. Ann.*, **58**, 1 (1896).

in wave length being accompanied by an increase in absorptive power. Moreover, Drude has shown that anomalous absorption goes hand in hand with anomalous dispersion ; that is to say, the refractive index decreases with decreasing wave length. As examples we may take glycerine and amyl alcohol.

	E.	n^2	
	$\lambda = \infty$	$\lambda = 2$ metres.[6]	$\lambda = 0\cdot 73$ metres.[3]
Glycerine . .	$56\cdot 2$ [1]	$39\cdot 1$	$25\cdot 4$
Amyl alcohol .	$15\cdot 05$ [2]	$10\cdot 8$	$5\cdot 51$

§ 3. *THE EXPERIMENTAL DETECTION OF ABSORPTION*

The usual method[4] of examining the behaviour of liquids in the presence of electric waves requires large quantities of the substance, and so is rendered of little value for general application to organic compounds. Drude[5] designed an apparatus which requires only a small quantity—less than one cubic centimetre—of the material, so that he was able to examine a large number of scarce compounds. A brief description of Drude's apparatus will make somewhat clearer the meaning of the data which we shall later examine. Since the absorptive power varies with wave length, it is necessary to choose vibration of known period as a standard for the comparison of different substances. Drude constructed his apparatus of such dimensions as to give waves of about 72 centimetres in length, or a frequency of 400×10^6 per second. At this high frequency normal substances of small conductivity show no absorption.

[1] Thwing, *Zeit. Phys. Chem.*, **14**, 286 (1894).
[2] Tereschin, *Wied. Ann.*, **36**, 792 (1889).
[3] *Wied. Ann.*, **58**, 1 (1896).
[4] Arons and Rubens, *Wied. Ann.*, **42**, 581 (1891)
[5] *Ber.*, **30**, 940 (1897) ; *Zeit. Phys. Chem.*, **23**, 280 (1897).

The apparatus consists essentially (see Fig. 34) of the primary system AA connected with the terminals of an induction coil, and surrounded by the secondary leads BB. The latter, after being bent twice at right angles, are prolonged parallel to one another for 10·5 centimetres at a distance of two centimetres apart. Each of the parallel wires is fused into a small brass tube, C, 25 centimetres long. Into the other ends of these tubes are fitted two copper wires, D, D, which are attached at their further end to a vulcanite holder, G, provided with a handle. By this arrangement D, D can be moved in and out of the brass tubes. Three and a half centimetres in front of the two tubes a bridge, E, is placed and connected to the earth, and the bridge F is laid across the wires DD just
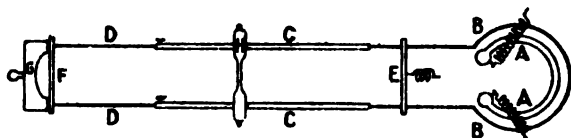
FIG. 34.

in front of the vulcanite holder. When the coil is in action, electric oscillations are produced in the system in front of E. To bring the two systems before and behind E into resonance with one another it is only necessary to adjust the distance from E to F ; this is done by moving D, D in or out of C, C. When resonance is established F becomes a nodal point, and the distance from E to F will be equal to half a wave length or, in this apparatus, 36 centimetres. Other similar points can be found at 72, 108, etc., cms. from E. The best way of detecting the resonance of the two systems is to place a vacuum tube, H, on the wires C, C about 16 centimetres or a quarter wave length behind E ; at resonance the tube lights up strongly and F is adjusted till the maximum glow is attained.

The liquid to be examined is contained in a small flask of ¼ c.cm. capacity with platinum wires fused in on opposite sides. After the apparatus has been adjusted to resonance the metal

bridge at F is replaced by the flask containing the substance. If the latter is non-absorbent the waves are totally reflected at F, and on adjusting F, E points are found where the tube glows as brightly as before. If, however, the liquid is absorbent the amplitude of vibration becomes weakened after reflexion from F, and the maximum glow in the tube correspondingly dimmer. At the same time the nodal points which can be detected become fewer, in fact with strong absorbents it is hard to find even the first position of resonance. As might be expected, the absorptive power of different substances varies considerably, and therefore in qualitative measurements Drude distinguished between four degrees of absorption : very weak, weak, strong, and very strong, according to the brightness of maximum glow in the tube.

Quantitative measurements can be obtained by finding the conductivity of a solution of an electrolyte or any normal absorbent which exerts an absorption equal in strength to that of the substance under examination. The index of absorption of the standard is then calculated from equation (iii) in § 2, and the value obtained is equal to the absorption index of the substance.

The absorptive index of aqueous sodium chloride has been measured by Drude.

<div align="center">TABLE I.</div>

<div align="center">$NaCl + H_2O$.</div>

p	x	p	x	p	x
0·045	0·025	0·99	0·37	3·88	0·71
0·21	0·111	1·29	0·44	8·25	0·83
0·50	0·219	1·69	0·51	25·0	0·91
0·70	0·289	2·06	0·57		

In the table, the columns under p show the number of grams of sodium chloride contained in 100 grams of the solution.

The apparatus, with certain modifications, can be used for measuring the electric index of refraction and dielectric

constant; but for a description of the method, the reader is referred to Drude's [1] original papers.

It should be noticed that, as a general rule, anomalous absorption decreases with increase of temperature. For example, amyl alcohol exerts "very strong" absorption at 20°, but is "weak" at 85° C. Similarly, glycerine is "weak" at 85°, and "very strong" at 20°. In both cases the heated liquids assume the original absorption on cooling.

§ 4. ANOMALOUS ELECTRIC ABSORPTION AND CHEMICAL CONSTITUTION

During the investigation of the nature of anomalous absorption, Drude's attention was drawn to the fact that an alcohol exerts strong absorption, whilst the isomeric ether is non-absorbent. This seemed to indicate that anomalous absorptive power is determined by the constitution of the substance, and the surmise was confirmed by further experiment. It was found that all alcohols are absorbent. Examination of a wider range of material showed that, with the exception of water, all compounds containing hydroxyl exert anomalous absorption, and, as a rule, those which do not contain hydroxyl are non-absorbent. Anomalous absorption thus seems to be conditioned by the presence of hydroxyl in the molecule. The evidence [2] from which Drude established this relation is summarized in the following list of non-absorbent and absorbent media.

TABLE II.

NON-ABSORBENTS. $\lambda = 73$ cm.

Ethers.	Esters of benzoic acid.	Aromatic hydrocarbons.
Esters of formic acid.	,, inorganic	Acid chlorides.
,, acetic acid.	acids.	Chloral.
,, higher fatty	Ketones.	Chloroform.
acids.	Aldehydes.	Carbon tetrachloride.
Phthalide.	Acetal.	Water.

[1] *Wied. Ann.*, **55**, 633 (1895); **58**, 1 (1896); **59**, 17 (1896); **60**, 50 (1897); *Zeit. Phys. Chem.*, **23**, 282 (1897).

[2] *Ber.*, **30**, 940 (1897); *Zeit. Phys. Chem.*, **23**, 308 (1897).

TABLE III.

ABSORBENTS. $\lambda = 75$ cm.

Substance.	Absorption.	x	Substance.	Absorption.	x
Methyl alcohol .	Weak	0·08	Formic acid . .	Weak	0·08
Ethyl alcohol. .	Very strong	0·21	Acetic acid . .	,,	0·07
Propyl alcohol .	,,	0·41	Propionic acid .	Very weak	0·03
Isopropyl alcohol	,,	0·24	Butyric acid . .	,,	0·02
Butyl alcohol . .	,,	0·45	Isobutyric acid .	,,	—
Isobutyl alcohol .	,,	0·47	Valerianic acid .	,,	0·02
Amyl alcohol .	,,	0·43	Isovalerianic acid	,,	—
Heptyl alcohol .	,,	0·31	Lactic acid . .	Strong	0·25
Allyl alcohol . .	Weak	0·07	Chloral hydrate.	Weak	0·03
Glycerine . . .	Very strong	0·42	Benzaldoxime .	,,	0·06

Drude has further pointed out that anomalous absorption is to a certain extent controlled by the dielectric constant of the medium, a low dielectric constant being accompanied by a weak absorptive power. For example, the fatty acids have low dielectric constants and weak absorptive power in contrast with the alcohols, which are stronger absorbents and possess higher dielectric constants.

TABLE IV.

Alcohols.	E	x	x	E	Acids.
Ethyl alcohol.	26·0	0·21	0·07	10·0	Acetic acid
Propyl alcohol	22·4	0·41	0·03	5·5	Propionic acid
Butyl alcohol.	19·2	0·45	0·02	3·0	Butyric acid

The influence of dielectric constant is further illustrated by the fact that a mixture of a fatty acid with a non-absorbent of high dielectric constant shows strong absorption; *e.g.* pure butyric acid absorbs "very weakly," but a concentrated aqueous solution exerts "strong" absorption.

It is probable that absorptive power is further influenced by molecular weight, since in homologous series the absorption

index rises with additional methylene groups; but it will be observed in the examples quoted below that the increase on passing from member to member is not constant.

TABLE V.

Substance.	x	E	Substance.	x	E
Methyl alcohol[1] .	0·08	35·3	Isopropyl alcohol	0·24	2·6
Ethyl alcohol . .	0·21	26·0	Isobutyl alcohol .	0·47	18·8
n. Propyl alcohol .	0·41	22·4	Isoamyl alcohol .	0·43	16·7
n. Butyl alcohol .	0·45	19·2	Sec. butyl alcohol	0·33	15·5
n. Heptyl alcohol	0·31	6·6	Tert. butyl alcohol	0·40	11·4

This behaviour is not shown by all homologous series, for the effect of a small and continually decreasing dielectric constant may overcome that of rising molecular weight.   In the normal fatty acids there is a slight fall in the value

TABLE VI.

Substance.	x	E
Formic acid[1] . . .	0·08	62·0
Acetic acid . . .	0·07	10·0
Propionic acid . .	0·03	5·5
Butyric acid . . .	0·02	3·0
Valerianic acid . .	0·02	3·0

of x on ascending the series, and it will be noticed that E is small, whereas with the alcohols it is relatively large, and remains at about the same value, heptyl alcohol excepted. Generally speaking, solids have very low dielectric constants, and hence the absorptive power of a liquid hydroxylic compound may be lessened or entirely removed by solidification; for example, chloral hydrate, in the super-cooled state, absorbs strongly, but on crystallization the absorption disappears.

[1] As with other physical properties, the initial members of these series are abnormal and may be omitted from consideration.

On reviewing all the available data, it seems almost certain that there are other groups besides hydroxyl which favour anomalous electric absorption. There are many compounds which do not contain hydroxyl and are yet absorbent. The following list of these substances has been collected from the observations of Drude [1] and of Kauffmann.[2]

TABLE VII.

Substance.	Absorption.	x	Substance.	Absorption.	x
Ethyl cyanacetate .	Weak	0·06	α Nitronaphthalene		
,, cinnamate .	,,	0·08	(fused) . . .	Weak	—
,, aconitate. .	Strong	0·19	*o.* Nitrobenzalde-		
,, salicylic ethyl			hyde (fused). .	Strong	—
ester	Weak	0·07	Ethyl *o.* nitrocin-		
Ethyl phenyl ketone	,,	0·04	namate (fused) .	,,	—
Monobromonaphtha-			Dinitrotoluene		
lene	,,	0·05	(fused) . . .	,,	—
Azoxybenzene			Dinitro bromo ben-		
(fused) . . .	Strong	—	zene (fused) . .	Moderate	—
Acetanilide (fused) .	,,	—	Benzil (fused) . .	Strong	—
Benzylideneaniline .	,,	—	Benzamide (fused) .	,,	—
Nitrobenzene . .	Weak	0·05	Anisidine . . .	Weak	—
Aniline	Very weak	—	Benzonitrile . .	Very weak	—
Benzaldehyde . .	,,	—	Benzyl cyanide. .	,,	—
Furfurane . . .	,,	—	Phenylacetaldehyde	,,	—

The lower portion of the table contains a few substances whose absorption may be regarded as doubtful on account of its weakness. It is clear, then, that the exact relations between absorption and chemical constitution are not yet known, but from the above examples it seems that the nitro group and the ethylenic linkage favour anomalous absorption. The attempt of Kauffmann[2] to connect this property with the reactivity of the molecule correlates a number of these exceptional cases, and it is therefore worth attention. Kauffmann claims to have established the law that the molecules of

[1] *Zeit. Phys. Chem.*, **23**, 308 (1897).
[2] *Zeit. Phys. Chem.*, **28**, 673 (1899).

all dielectric substances which absorb vibrations of 75 cm. wave length contain a "loose bond." In the alcohols, the "loose bond" is to be found between the oxygen and hydrogen of the hydroxyl group. As further examples of absorbent substances containing a "loose bond," we may take the esters of certain carboxylic acids which, under suitable conditions, decompose, losing carbon dioxide. Thus, as we have seen, ethyl benzal-malonate is absorbent; the free acid fuses at 195° with evolution of carbonic acid and formation of cinnamic acid—

$$C_6H_5CH=C(COOH)_2 \rightarrow CO_2 + C_6H_5CH=CHCOOH$$

and the ester decomposes in a similar manner when boiled with strong alcoholic potash. Further, it is found that the following esters of acids containing two carboxyl groups united to the same carbon atom are absorbent, and it will be remembered that acids of this type readily lose carbonic acid. It

ISOALLYLENETETRACARBOXYLIC ETHYL ESTER.

$$(H_5C_2OOC)_2C(CH_2COOC_2H_5)_2 \quad x = 0.17.$$

m.p. of acid 150° with evolution of CO_2
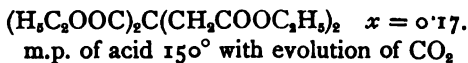
$\alpha\alpha'$ DIMETHYLDICARBOXYGLUTARIC ETHYL ESTER.

$$(H_5C_2OOC)_2C—CH_2—C(COOC_2H_5)_2 \quad x = 0.03$$
$$\qquad\quad |\qquad\qquad\quad |$$
$$\qquad\quad CH_3\qquad\quad CH_3$$
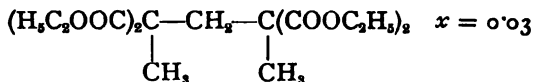
The acid decomposes at 100° in aqueous solution.

ETHYLDICARBOXYGLUTACENIC ESTER.

$$(H_5C_2OOC)_2C=CH—C(COOC_2H_5)_2 \text{ loses } CO_2 \text{ when saponified}$$
$$\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\quad C_2H_5 \qquad x = 0.03$$

α BENZYL α' ETHYL DICARBOXYGLUTARIC ESTER.

$$(H_5C_2OOC)_2C—CH_2—C(COOC_2H_5)_2 \quad x \text{ is very small}$$
$$\qquad\quad |\qquad\qquad\quad |$$
$$\qquad\quad CH_2C_6H_5 \quad C_2H_5 \qquad \text{acid loses } CO_2 \text{ below 100°}$$
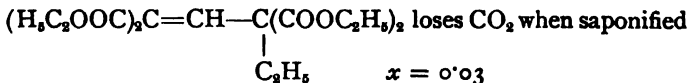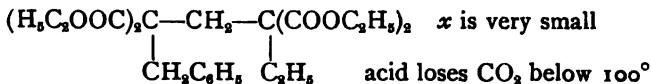
It may be noted that the ester of malonic acid, the simplest acid of this class, is non-absorbent, and is thus exceptional to Kauffmann's rule. From this and other instances which can be found by consulting the previous lists, it is clear that the relation is far from being universally true.

It must be admitted that the relations hitherto discovered between anomalous absorption and chemical constitution are very indefinite. But this state of affairs is not surprising when it is remembered that the absorption of only one particular wave length has been studied. It is as though, instead of mapping out the complete absorption spectrum of a substance, we were to confine our attention to the intensity of absorption of one particular ray. There is no doubt that a more complete study of the electric absorption spectrum would yield interesting results.

§ 5. *APPLICATION OF ANOMALOUS ABSORPTION*
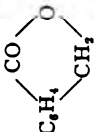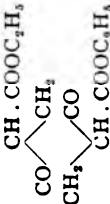
Since the anomalous absorption of compounds containing only carbon, hydrogen, and oxygen is in nearly every case accompanied by a hydroxyl group, and since substances which do not contain hydroxyl are non-absorbent, it is evident that we may employ this property to ascertain whether a compound contains this group. It is thus possible to detect the formation of a hydroxylic compound when a substance containing the carbonyl group is dissolved in water. For example, chloral is non-absorbent, but chloral hydrate absorbs strongly; hence the latter has the structure

$$-CH\begin{cases}OH\\OH\end{cases}$$
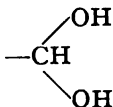
Moreover, since aqueous solutions of the non-absorbent acetaldehyde are absorbent,[1] we may infer that the aldehydrol is formed—

[1] Drude, *Zeit. Phys. Chem.*, **23**, 320 (1897).

TABLE VIII.

Substance.	Formula.	Condition.	Absorption.
Ethyl phenylacetate	$C_6H_5CH_2COOC_2H_5$	At 21°	None
Ethyl levulinate	$CH_3COCH_2CH_2COOC_2H_5$	At 21°	,,
Ethyl acetoacetate	$CH_3COCH_2COOC_2H_5$	At 6°	Weak
,,		At 80°	None
Phthalide	$C_6H_4 \genfrac{}{}{0pt}{}{CO}{CH_2} \!\!\diagdown\!\!\diagup O$	Fused	,,
		Super-cooled	Strong
Ethyl succinylosuccinate	$\genfrac{}{}{0pt}{}{CH.COOC_2H_5}{} \begin{smallmatrix} CO & CH_2 \\ CH_2 & CO \end{smallmatrix} \genfrac{}{}{0pt}{}{}{CH.COOC_2H_5}$	Fused, 130°	None
		Solid, 19°	,,
Diphenyl acetaldehyde	$(C_6H_5)_2CH.CHO$	—	Very strong
Ethyl oxaloacetate	$C_2H_5OOC.CO.CH_2.COOC_2H_5$	At 19°	,,
Ethyl oxalopropionate	$C_2H_5OOC.CO.CH{-}COOC_2H_5$ (CH_3)	At 19°	,,
Ethyl benzoylacetate	$C_6H_5COCH_2COOC_2H_5$	At -4°	,,
,,		At 20°	,,
,,		At 65°	Very weak
,,		At 75°	None

	Formula	Condition	Absorption
Ethyl oxymethylene acetoacetate	$CH_3COCCOOC_2H_5$ $\\ \ \ \ \ \|$ $CHOH$	At 6°	Very strong
,, ,,	,,	At 20°	Strong
		At 90°	Weak
Ethyl oxymethylene malonate	$HOCH=C(COOC_2H_5)_2$	At 19°	Strong
		At 90°	Weak
Ethyl oxymethylene phenylacetate	$HOCH=C—COOC_2H_5$ $\\ \ \ \ \ \ \ \ \|$ C_6H_5	At 20°	Very strong
Ethyl formyl phenylacetate	$OCH—CH—COOC_2H_5$ $\\ \ \ \ \ \ \ \ \ \|$ C_6H_5	At 20° (solid)	None
Benzoylacetone	$C_6H_5CO—CH_2COCH_3$	Fused and super-cooled	Very strong
		Solid	None
,, ,,	,,	At 45°	Weak
		At 80°	Very weak
Acetylacetone	$CH_3COCH_2COCH_3$	At 6°	Weak
		At 20°	Non-absorbent
,, ,,	,,	Solid	Weak
		At 90°	Strong
Dibenzoyl methane	$(C_6H_5CO)_2CH_2$	Super-cooled liquid	Very strong
Ethyl isoaconitate	$(C_2H_5OOC)_2CH—CH=CH.COOC_2H_5$	Fresh at 20°	Strong
,, ,,	,,	Two years old at 20°	,,
,, ,,	,,	Five years old at 20°	None

$$\dot{C}H_3CHO + H_2O \rightarrow CH_3CH(OH)_2$$
$$\text{Aldehydrol}$$
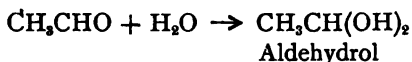
and this conclusion is confirmed by magnetic rotation[1] and refractive index.[2]   Moreover, by cooling the solution, Colles has isolated the compound $C_2H_4O \cdot H_2O$.   The method is particularly adapted to the study of tautomeric substances, whose structure may vary according to conditions between —CH_2—CO— and —CH=C . OH—.

Evidently if a given specimen of such a compound exert absorption, it probably contains a certain quantity of the enolic tautomeride, whilst if it be non-absorbent the absence of this form may be inferred.   The method cannot, of course, be applied to substances which contain other hydroxyl groups in the molecule, since in these cases either form would show anomalous absorption.   The chief results obtained by Drude[4] are shown in the foregoing table (VIII.).

The results are not so easy to interpret as might appear at first sight, since it must be remembered that temperature and the passage from solid to liquid state have an influence on absorption independent of that exerted by constitution.   Rise in temperature decreases absorption, whilst the influence of physical state is at present uncertain, but it seems to depend on the dielectric constant.

Nevertheless, after making allowance for these factors, we see that rise in temperature favours the change of the enolic to the ketonic form, and this in certain cases is confirmed by other physical methods.   The effect of physical state is so obscure that we are not justified in concluding that the solids which are quoted as non-absorbent do not contain any of the enolic tautomeride.

We will not pause to consider each example quoted in the table, but it may be observed that, generally speaking, the results are in accord with chemical experience and other

[1] Perkin, *Trans. Chem. Soc.*, **51**, 808 (1887).
[2] Miss Homfray, *Trans. Chem. Soc.*, **87**, 1435 (1905).
[3] *Trans. Chem. Soc.*, **89**, 1250 (1906).
[4] *Ber.*, **30**, 940 (1897).

physical data. The case of acetoacetic ester is interesting since the magnetic rotation and refractive index of this substance show it to be purely ketonic at ordinary temperatures, whilst according to anomalous absorption a small quantity of the enolic tautomeride is present. This is possibly due to the age of the specimens examined; for, when fresh, the substance may contain the enolic form. The effect of age can be seen with ethyl isaconitate which, if freshly distilled, is strongly absorbent, but when left undisturbed for five years becomes non-absorbent, and is then evidently the pure carbethoxy form—

$$(H_5C_2OOC)_2CH—CH=CH—COOC_2H_5$$

The absorption of the fresh specimen is evidently due to the presence of the hydroxylic isomeride—

$$(C_2H_5OOC)C—CH=CH—COOC_2H_5$$
$$HO . \overset{\|}{C}—OC_2H_5$$
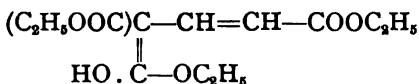
CHAPTER XV

CONCLUSION

In the first chapter the development of the relations between chemical composition and physical properties was traced side by side with the advance of chemical science. It was then observed that until recent years the growth of our subject had always been dependent on the advancement of the chemical theories of the structure of compounds.

Those interested solely in the chemical aspect of the subject will naturally be inclined to ask whether their science has really benefited by the innumerable empirical relations which have been established between physical properties and constitution. So far as the practical side is concerned, the chemist has obtained many advantages. The majority of the physical properties dealt with in this volume may be turned to some use in obtaining information of the structure of a substance ; and, where chemical evidence is wanting, the information is particularly welcome. But whether entire faith can be placed in the constitution of a substance as determined by physical methods must, even under the best of conditions, be open to some little doubt. The reliability of the conclusion depends on the circumstances attending the case, and here the factors of prime importance are the accuracy with which the physical property can be measured, and the scope of the data on which the empirical law is based.

It is clear that the various physical properties greatly differ in chemical utility. Of all those which have been recommended for the purpose, there is no doubt that absorption spectra, refractive, dispersive, and magnetic rotatory power give the

more reliable information ; but even these require to be very carefully handled. Since the application of each of these properties has been very fully described in former chapters, it is unnecessary here to describe the precautions required in using them ; but it may be observed that fortunately the latitudes of application in refractive power and absorption spectra are to a certain extent complementary. Refractive power is more reliable when applied to bodies of fairly simple constitution ; but with complex substances the conclusions become uncertain. On the other hand, Hartley's method of applying absorption spectra to determining constitution cannot be used for very simple compounds, but it is remarkably successful with substances of intricate structure. Capillarity and viscosity admirably serve to detect the formation of complex molecules by association or combination with a solvent. Also molecular volume yields information on this point.

There are, indeed, a few chemists who are inclined to distrust entirely the physical method of determining constitution ; but the majority seem ready to accept its evidence when strictly subordinated to chemical. It cannot be denied that at the other extreme are a few enthusiasts who are prepared to throw aside chemical fact if it should not accord with the physical results. But there is no doubt that on this question, as on many others, the opinion of the average chemist is the soundest.

The practical application of the physical properties seems of minor importance when compared with the bearing which they have, or are likely to have, on chemical theory. Before approaching this question we must return for a moment to the development of the relations between the two sciences.

Until the end of last century the structural theory of organic compounds remained in the condition in which it had been left by Kekulé. Nevertheless many instances had been collected showing that the usual method of picturing the molecule of unsaturated substances was not altogether satisfactory, since it did not afford a complete explanation of the behaviour of these compounds. Fresh ground was then broken by Thiele[1] who discovered in his own observations and those

[1] Thiele, *Ann.*, **306**, 87 (1899) ; **308**, 333 (1899) ; **319**, 129 (1907).

of Fittig, von Baeyer, and of Harries, some general rules governing the behaviour of unsaturated carbon compounds, and these could not be explained by the structure theory in its current form. Thiele adduced a large number of examples to show that substances containing adjacent unsaturated linkages behave abnormally with additive reagents. For example, the double ethylenic system in compounds of the type

$$RCH{=}CH{-}CH{=}CHR$$

frequently behaves towards additive reagents as though it contained only one ethylenic bond ; moreover, the reagent becomes attached to the end carbon atoms of the system instead of to either pair of adjacent atoms, the product being

$$\begin{array}{ccc} RCH{-}CH{=}CH{-}CHR \\ | & | \\ X & X \end{array}$$

and not

$$\begin{array}{cc} RCH{-}CH{-}CH{=}CHR \\ | & | \\ X & X \end{array}$$
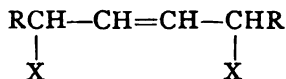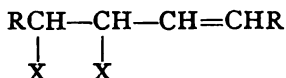
In some cases the process of addition may proceed a stage further, to the saturated compound ; but the chief peculiarity of these substances is that the activity of the central carbon atoms is abnormally low. In giving an explanation of this behaviour Thiele had recourse to a theory of residual affinity. He retained the usual assumption that unsaturated carbon atoms are united by more than one valency unit; but he added thereto the notion that such atoms possess a residue of affinity or " partial valency." The inactivity of the central carbon of the system is readily explained by assuming that their residual affinities satisfy each other, the ethylenic bonds becoming " conjugated."

The condition of the group may be represented by the formula

$$RCH{=}CH{-}CH{=}CHR$$
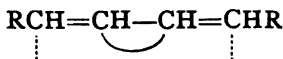
in which the dotted lines represent the free partial valencies

and the curved line the pair that satisfy each other. The hypothesis clearly explains the inactivity of the central carbon atoms.

Now, since there are many exceptions [1] to the rule governing the additive reactions of these substances, it is clear that Thiele's conception is only a first approximation to the truth. From the point of view of general structural theory, the most interesting aspect of the hypothesis is that it contains a definite expression of how unsaturated groups may influence one another. The notion of residual affinity was not by any means a new one, for chemists had long been aware of its existence, although they had shrunk from freely applying it to explain chemical facts. The credit for the earliest application of the idea to organic chemistry lies with Armstrong,[2] Collie,[3] Claus,[4] and Nef.[5] The latter-named chemists studied the nature of unsaturated carbon from a general standpoint, while Armstrong and Collie dealt mainly with the problem of substitution in the benzene nucleus.

The development of the hypothesis of residual affinity seems to mark a new epoch in organic chemistry, which may be said to have been firmly established by the researches of Thiele. There is no doubt that the importance which Thiele's hypothesis has assumed is due to the fact that it was accompanied by a method of formulation which enabled the idea to be grafted on to the current formulæ.

During the following years a few experimenters showed that the relative positions of unsaturated atoms or groups may influence the physical as well as the chemical properties of a substance. It was first shown by W. H. Perkin, Sen.,[6] that the magnetic rotation and refractive power of aromatic compounds is influenced by the relative situations of the benzene

[1] See Meyer and Jacobson, *Lehrbuch der Org. Chem.*, I. part 1, 796 (1907).

[2] *Trans. Chem. Soc.*, **51**, 264 (1887).

[3] *Trans. Chem. Soc.*, **71**, 1013 (1897).

[4] *Ber.*, **14**, 432 (1881).

[5] *Ann.*, **270**, 267 (1892) ; **280**, 291 (1894) ; **287**, 265 (1895) ; **298**, 202 (1897) ; **309**, 264 (1899).

[6] *Trans. Chem. Soc.*, **69**, 1141 (1896).

nucleus and an unsaturated group in a side chain.   Later the
same chemist attributed[1] the abnormally high rotation of
$\Delta^{3.8(9)}$ *p*. menthadiene
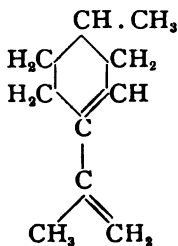
$\Delta^{3.8(9)}$ Menthadiene.   Limonene.
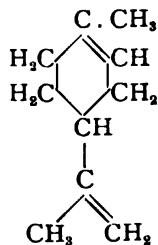
M rot. = 13·06.   M rot. = 11·24.

to the peculiar position occupied by the double linkage.   Also
Muller and Bauer[2] clearly expressed a similar view of the
effect of " negative " groups on refractive power ; but it was not
until quite recently that any comprehensive observations on the
subject were made.   For many years Brühl had been aware of
some peculiarities in the dispersive and refractive power of
unsaturated compounds, and by the accumulation of sufficient
data he was now able to show[3] that if unsaturated groups are
directly united to one another the numerical values of these
properties become abnormal.   When, however, the unsaturated
atoms are separated by saturated groups the property has
a normal value.   It is important to notice that this general-
ization is not confined to the ethylenic arrangement, but
embraces the inorganic hydroxyl, amino, nitro, and nitroso
groups.   Moreover, Brühl extended the connotation of the
term " conjugated " to any system of unsaturated groups whose
residual affinities exert a mutual influence ; whilst Thiele seems
to have applied it solely to unsaturated carbon.   Within a short
time after the publication of these results, research was extended

[1]   *Trans. Chem. Soc.*, **89**, 854 (1906).
[2]   *Bull. Soc. Chim.*, **27**, 1014 (1902).
[3]   *Ber.*, **40**, 878 (1907).

to other physical properties. Sir W. H. Perkin then pursued[1] his observations on magnetic rotatory anomaly with hexatriene and derivatives of the allied compound benzene. The results showed that the propinquity of unsaturated groups is responsible for the anomaly. But a noteworthy difference between this property and refractive power was discovered; since the magnetic rotation anomaly does not entirely disappear if a saturated group be inserted as a screen between the unsaturated atoms, whereas with refractive power a single intervening group is usually sufficient to remove the anomaly. In fact, Perkin's studies of magnetic rotation seem to show that unsaturated groups may influence one another even if they are not immediately attached.

The mutual influence of unsaturated groups also has been demonstrated with the aid of absorption spectra. Armstrong[2] was the first to suggest that the co-operation of unsaturated groups may give rise to colour. Then Baly and Collie, in their study[3] of the absorption spectra of aromatic compounds, were able to show that if an unsaturated group is attached to the benzene nucleus the characteristic spectrum of the latter is destroyed. Further evidence can be adduced from their work to show the effect of inserting saturated groups between the nucleus and the unsaturated atom. Stewart and Baly then discovered from the reactivity and absorption spectra of a diketones that adjacent carbonyl groups exert an influence on one another.

Optical rotatory power has been brought into line with the afore-mentioned properties. From time to time many isolated observations have been made on the influence of conjugated unsaturation on this property, but the systematic work of Hilditch[4] is the chief source of information. The following list of d. camphoryl and l. amyl thio derivatives affords illustration of the effect in question.

[1] *Trans. Chem. Soc.*, **91**, 806 (1907).
[2] *Proc. Chem. Soc.*, **9**, 577 (1893); *Encyclopaedia Britannica*, **26**, 746 (1902); Armstrong and Robertson, *Trans. Chem. Soc.*, **87**, 1276 (1905).
[3] *Trans. Chem. Soc.*, **87**, 1332 (1905).
[4] *Trans. Chem. Soc.*, **93**, 1388, 1618 (1909); **95**, 331 (1909).

TABLE I.

Substance.	Formula.	Molecular rotation.
d. Camphoryl mercaptan .	$C_{10}H_{15}O.SH$	$+ 11°$
d. Camphoryl disulphide .	$(C_{10}H_{15}OS_2)_2$	-355
d. Camphoryl α disulphone	$(C_{10}H_{15}OSO_2)_2$ . . .	$+132$
l. Amyl disulphide . . .	$(C_5H_{11}S)_2$	*circ.* -149
l. Amyl sulphide . . .	$(C_5H_{11})_2S$	,, -42
l. Amyl sulphone . . .	$(C_5H_{11})_2SO_2$	,, -34
α Mercapto-propionic acid.	$CH_3CH(SH)COOH$ . .	-45.5
α Thio-propionic acid . .	$[CH_3(COOH)CH]_2S$ . .	-190.0
α Dithio-propionic acid .	$[CH_3(COOH)CH—S]_2$.	-429.0

On referring to the table it will be seen that camphoryl mercaptan has the feeble molecular rotation of 11° ; but this is greatly increased by uniting the unsaturated sulphur atoms, and again diminished on saturating them by conversion to sulphone groups. Similar relations are exhibited by the amyl and thio-lactic derivatives. More striking illustrations of this principle are to be found in the derivatives of imino and methylene camphor. The observations are due to Forster[1] and to Haller.[2] From the examples which are given it is evident that the occurrence of the conjugated groupings

$$—C=N—$$
$$|$$
$$—C=O$$
and
$$—C=C<$$
$$|$$
$$—C=O$$
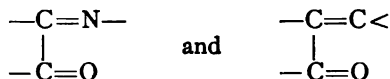
cause an increase in rotatory power and the effect is greatly enhanced by the association of an aromatic nucleus with either system.

$$C_8H_{14}\left\langle\begin{array}{c}CH.NH_2\\|\\CO\end{array}\right.$$
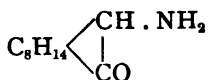
Amino camphor.
$(M)_d = 35°.$

$$C_8H_{14}\left\langle\begin{array}{c}C=NH\\|\\C=O\end{array}\right.$$
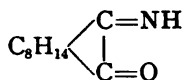
Imino camphor.
$(M)_d = 151°.$

[1] Forster, *Trans. Chem. Soc.*, **95**, 942 (1909).

[2] Haller, *Compt. Rend.*, **128**, 1370 (1899) ; **736**, 1222 (1903) ; Haller and Müller, *Compt. Rend.*, **129**, 1006 (1899).

$$C_8H_{14} \overset{CHNHC_6H_5}{\underset{CO}{\diagup\!\!\Big|\!\!\diagdown}}$$
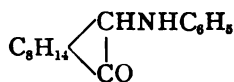
Phenylamino camphor.
$(M)_d = 309°.$

$$C_8H_{14} \overset{C=N \cdot C_6H_5}{\underset{CO}{\diagup\!\!\Big|\!\!\diagdown}}$$
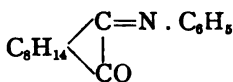
Phenylimino camphor.
$(M)_d = 1750°.$

$$C_8H_{14} \overset{CH \cdot CH_3}{\underset{CO}{\diagup\!\!\Big|\!\!\diagdown}}$$
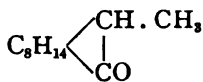
Methyl camphor.
$(M)_d = 50°.$

$$C_8H_{14} \overset{C=CH_2}{\underset{CO}{\diagup\!\!\Big|\!\!\diagdown}}$$
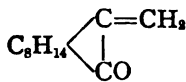
Methylene camphor.
$(M)_d = 209°.$

$$C_8H_{14} \overset{CH \cdot CH_2C_6H_5}{\underset{CO}{\diagup\!\!\Big|\!\!\diagdown}}$$
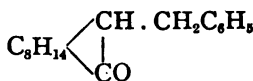
Benzyl camphor.
$(M)_d = 248°.$

$$C_8H_{14} \overset{C=CHC_6H_5}{\underset{CO}{\diagup\!\!\Big|\!\!\diagdown}}$$
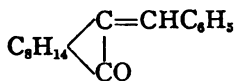
Benzylidene camphor.
$(M)_d = 1020°.$

The most remarkable case is that of phenylene bis-imino camphor, which has molecular rotation of over six thousand degrees.

$$C_8H_{14} \overset{C=N \cdot C_6H_4 \cdot N=C}{\underset{CO \qquad\qquad OC}{\diagup\!\!\Big|\!\!\diagdown\;\;\diagup\!\!\Big|\!\!\diagdown}} C_8H_{14} \qquad (M)_d = 6100°$$
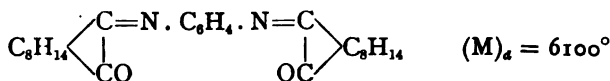
At the present time the influence of conjugation has not yet been examined with other physical properties than these; but the observations of Auwers and Van der Heyden [1] seem to indicate that some relationship exists with volatility and density. With the chloro-ketones of the structures:

$$\begin{array}{c} CH_3 \diagdown \quad \diagup CHCl_2 \\ C \\ HC \qquad CO \\ \| \qquad | \\ HC \qquad CH_2 \\ \diagdown CH \diagup \\ | \\ R \end{array}$$

$$\begin{array}{c} CH_3 \diagdown \quad \diagup CHCl_2 \\ C \\ H_2C \qquad CO \\ | \qquad | \\ H_2C \qquad CH \\ \diagdown C \diagup \\ | \\ R \end{array}$$
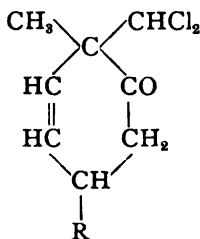
R = alkyl group.
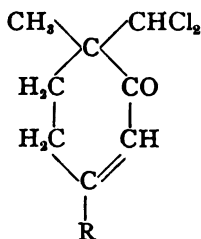
I.   II.

[1] *Ber.*, **41**, 2404 (1909).

the conjugated isomeride (II.) has uniformly the greater density, boiling-point, and refractive and dispersive powers. The data are collected in the following table.

TABLE II.

Substance.	B.P.	D_4^{20}	$\mathfrak{M}_\alpha$	$\mathfrak{M}_\gamma - \mathfrak{M}_\alpha$
$R = CH_3$ { I. structure .	125°	1·202	50·43	1·46
II. ,, .	151	1·227	51·41	1·86
$R = C_2H_5$ { I. ,, .	137	1·167	55·63	1·65
II. ,, .	161	1·194	56·06	2·03
$R = C_3H_7$ { I. ,, .	148	1·140	60·34	1·75
II. ,, .	168	1·162	60·63	2·18

After surveying the results of these researches it will be admitted that the study of physical properties has confirmed the hypothesis of mutual influence of residual affinities; moreover the results justify the extension of the hypothesis from unsaturated carbon to any other unsaturated atom. We may now briefly consider the most recent form taken by the development of these theories. Although most chemists are ready to admit that unsaturated atoms when directly united exert some influence on one another beyond that expressed in the usual formulæ, the question whether the residual affinities of atoms in other positions have such influence has not been definitely raised. The opinion that some action of this sort may take place seems, indeed, to have been generally entertained, but the sole definite illustration is the case of di-methyl pyrone. Collie showed that in this substance the bridge-oxygen and carbonyl groups are in some way connected, and he was able to represent the state of affairs with the usual method of formulation :

$$CH_3 . C \overset{\displaystyle{O}}{\underset{\displaystyle{HC \quad O \quad CH}}{\diagup\diagdown}} C . CH_3$$
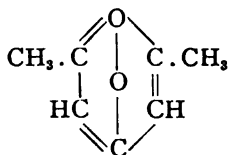
Physical properties throw some light also on this question. We have already noticed that Sir W. H. Perkin found that the magneto-optical anomaly of aromatic compounds persists even if the aromatic nucleus and unsaturated substituent be separated by saturated groups; and further data showing the distant action of residual-affinities have been given in the chapter dealing with magnetic rotatory power. By means of absorption spectra Baly and Stewart have been enabled to detect[1] the mutual influence of the carbonyl groups in diketohexamethylene.

$$
\begin{array}{c}
\diagup\mathrm{CO}\diagdown \\
\mathrm{CH_2} \qquad \mathrm{CH_2} \\
| \qquad\qquad | \\
\mathrm{CH_2} \qquad \mathrm{CH_2} \\
\diagdown\mathrm{CO}\diagup
\end{array}
$$
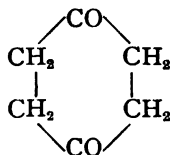
With refractive power the anomalous state of distant groups is not so readily detected, but it can be clearly observed[2] when three or more unsaturated groups are accumulated around a central saturated atom. Moreover, with the aid of this property and chemical activity, Clarke and Smiles claim to have shown[3] the connection between the sulphur and bridge-oxygen in the cyclic thioxane derivative:

$$
\begin{array}{c}
\diagup\mathrm{O}\diagdown \\
\mathrm{EtOCH} \qquad \mathrm{CHOEt} \\
| \qquad\qquad\quad | \\
\mathrm{CH_2} \qquad \mathrm{CH_2} \\
\diagdown\mathrm{S}\diagup
\end{array}
\qquad\qquad
\mathrm{C_6H_5{-}S{-}C_6H}
$$
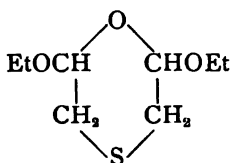
Diethoxythioxane.   Diphenyl sulphide.
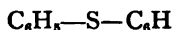
$\Delta = +0\cdot40.$ $\Delta = +1\cdot31.$

This substance has a slight exaltation of about 0·4 units and the additive capacity of the sulphur is abnormally low; in fact, the conditions are parallel to those obtaining in unsaturated sulphur compounds in which the sulphur atom is adjacent

[1] Stewart, *Stereochemistry*, this series, p. 485.
[2] See p. 301.
[3] *Trans. Chem. Soc.*, **95**, 992 (1909).

to unsaturated groups. For example, diphenyl sulphide has subnormal activity and an exaltation of about 1·3 units. It seems probable that a similar condition exists in N. alkyl derivatives of morpholine :

R
.
N
CH₂   CH₂
CH₂   CH₂
O
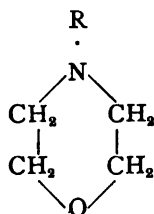
N. Alkyl morpholine.

R
.
N
CH₂   CH₂
HOCH₂   CH₂OH
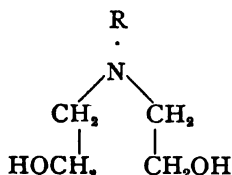
N. Alkyl diethanolamine.

since the refractive power[1] of these compounds is abnormal. The optical data from three members of this group are collected in the following table.

TABLE III.

Substance.	$\mathfrak{M}_D$ (obs.).	$\mathfrak{M}_D$ (calc.).	Δ
Morpholine	23·54	23·56	+0·02
N. Methyl morpholine .	29·01	28·40	+0·61
N. Ethyl morpholine . .	33·75	32·91	+0·84
Diethanolamine . . .	27·02	—	
Methyl diethanolamine .	31·86	—	
Ethyl diethanolamine . .	36·37	—	

The calculated values for $\mathfrak{M}_D$ were obtained by subtracting the atomic values of 2H and O′ from the molecular refractivities of the corresponding diethanolamines, allowance being made for the conversion of hydroxylic to ethereal oxygen. It should be observed that morpholine appears to be optically normal. It would be interesting to compare the chemical

[1] Knorr, *Ber.*, **30**, 918 (1897) ; **31**, 1071 (1898) ; *Ann.*, **301**, 1 (1898).

activity of these morpholine derivatives, but as yet this has not been done. In this connection we may notice that the additive capacity of sulphur in thio-diphenylamine (I.) is about the same as that of simple aromatic sulphides

I.   II.
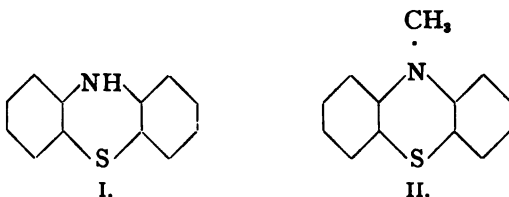
but when the basicity of the tervalent nitrogen is increased by alkylation (as in II.) the reactivity of the sulphur is remarkably diminished.

Very little is yet known of whether it is merely the spatial proximity of the unsaturated groups which permits the interaction of their residual affinities; but some information bearing on the question may be obtained from Miss Smedley's interesting work [1] on the refractive power of unsaturated ketones. The molecular refractivities of the *cis* and *trans* modifications of dibenzoyl-ethylene are different; that of the *trans* isomeride being the lower of the two and approaching more closely to the calculated value.

<div align="center">

Dibenzoyl-ethylenes.

</div>

$$CH-COC_6H_5$$
$$\|$$
$$CH-COC_6H_5$$

Cis form, M.P. 111°.

$\mathfrak{M}_\alpha = 74\cdot0$.

$$CH-COC_6H_5$$
$$\|$$
$$C_6H_5COCH$$

Trans form, M.P. 134°.

$\mathfrak{M}_\alpha = 71\cdot8$.

$\mathfrak{M}_\alpha$ (calc.) $= 70\cdot8$.
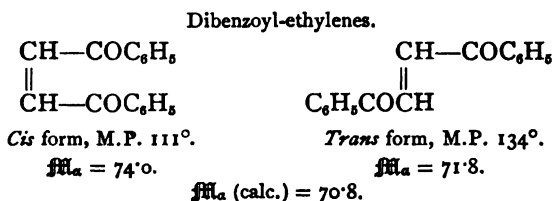
The increase in refractivity of the *cis*-isomeride seems to be due to a redistribution of the affinities of the two carbonyl groups. Miss Smedley represents this condition by a tendency to exist in the isomeric peroxide form :

[1] *Trans. Chem. Soc.*, **95**, 226 (1909).

$$CH-COC_6H_5$$
$$\parallel$$
$$CH-COC_6H_5$$

$\longrightarrow$

$\longleftarrow$

$$CH=C-C_6H_5$$
$$\mid$$
$$O$$
$$\mid$$
$$O$$
$$\mid$$
$$CH=C-C_6H_5$$

Peroxide form.
$\mathfrak{M}_\alpha$ (calc.) $= 83\cdot7$.
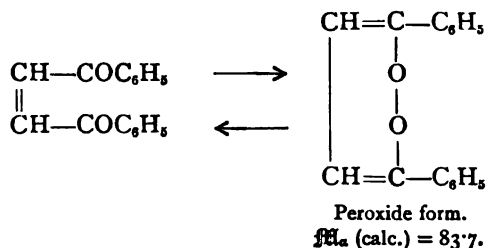
the substance being an equilibrium mixture of the two isomerides. The case is analogous to that of the α diketones which also tend to assume the peroxide structure.[1] It seems that in the *trans* form of dibenzoylethylene the carbonyl groups are so far apart that their affinities do not interfere with one another.[2]

The influence of spatial proximity of unsaturated groups can also be detected in optical rotatory power. The more interesting data [3] are collected in the following table.

TABLE IV.

DIMENTHYL ESTERS OF DIBASIC ACIDS.

Substance.	$(\alpha)_d$ 5 per cent. $CHCl_3$.	$(M)_D$ 5 per cent. $CHCl_3$.
Dimenthyl oxalate . . .	$-104\cdot0$	$-380\cdot6$
,, malonate . .	$-79\cdot2$	$-301\cdot1$
,, succinate . .	$-81\cdot9$	$-322\cdot7$
,, glutarate . .	$-80\cdot2$	$-328\cdot3$
,, adipate . .	$-83\cdot8$	$-353\cdot6$
,, pimelate . .	$-78\cdot3$	$-341\cdot5$
,, suberate . .	$-73\cdot5$	$-331\cdot1$
,, azelate. . .	$-72\cdot7$	$-337\cdot2$
,, sebacate . .	$-67\cdot1$	$-320\cdot6$

MENTHYL ESTERS OF KETONIC ACIDS.

Menthyl pyruvate . . .	$-83\cdot4$	$-188\cdot5$
,, acetoacetate . .	$-68\cdot3$	$-164\cdot1$
,, levulate . . .	$-67\cdot6$	$-171\cdot7$

[1] See p. 367.

[2] Also the refractivity of other stereoisomerides should be consulted, p. 304.

[3] Privately communicated by T. P. Hilditch.

In the two series quoted the initial members contain the carbonyl groups directly united to one another, and the esters of these acids have the highest rotation of the series. On ascending the series of dibasic acids the rotation of the esters at first falls and then rises to reach a maximum at the adipic ester, thence falling continually to the sebacic ester. Since optical rotatory power is very readily influenced by constitution it cannot be supposed that the position of the $>C=O$ groups is the sole factor which determines the relative activity of the members in this series. Nevertheless it is remarkable that the second maximum occurs in a substance containing the CO groups in the 1, 6 positions and, according to stereochemical theory, the carbon atoms at about this position (1, 5 or 1, 6) in a saturated chain are closely situated in space.

It must be observed that most of the researches in this direction have been more or less of a speculative nature; but the series of relations which we have now reviewed show that chemists' ideas on the question are assuming definite shape. On taking a general view of the trend of recent research it seems probable that the next development in the theory of organic chemistry will be the discovery of some generalization governing the mutual influence of unsaturated groups. There are abundant reasons for dissatisfaction with the present mode of formulation, and, although many successful attempts have been made to remove the discrepancies by introducing dynamic conceptions of the chemical molecule, it is clear that something more is needed. It is, however, very doubtful whether any advance can be made until our knowledge of the nature of chemical affinity and valency is very much more profound than it is at present. It seems almost impossible to solve the problem by means of chemical data alone, and for further help we must turn to the physical properties. The empirical relations between physical properties and chemical constitution, which form so large a portion of the matter in this book, are at present of very little value to us in the search after the nature of valency; but their turn will come when the relations between these properties and valency have been discovered. Very important researches in this field have already been commenced.

The chief line of advance has been made through the corpuscular theory of matter introduced by J. J. Thomson. According to this theory. valency must be regarded [1] as an electrical phenomenon. The affinity of an atom is occasioned by the instability of the system of corpuscles composing the atom. In order to attain a condition of stable equilibrium one or more " electrons " must be expelled from the system and the number of the electrons (or groups of electrons) which are thus rendered mobile determines the valency of the element. The mathematical development of this theory has been so far advanced that it is possible to obtain a relation between many of the optical properties of matter and the number of the mobile electrons present. Drude has shown how it is possible to calculate [2] from the dispersion of a substance the minimum number of mobile electrons which have free periods of vibration, and he has also found that the molecular values of this quantity can be represented as the sum of atomic values, which are approximately constant. A few of the atomic values are shown in the annexed table, and it will be seen that they roughly approach the valencies of the elements.

TABLE V.

Element.	P.	Element.	P.
Hydrogen . .	1·5	Carbon . .	3·7
Calcium . .	1·5	Silicon. . .	3·9
Oxygen. . .	2·7	Chlorine . .	6·2

P = number of electrons influencing the dispersion.

Hence the close relation between valency and the dispersional electrons seems demonstrated. It may be observed that since many simplifying assumptions have to be made in the calculation, a closer agreement between the values of P and the valencies can hardly be expected. Moreover,

[1] For further information the reader should refer to *Theory of Valency,* Dr. Friend, this series, 1909.

[2] The non-mathematical reader will find the whole subject excellently treated in *Modern Electrical Theory,* N. R. Campbell, Camb. Univ. Press, 1907.

Erfle has shown that the atomic values of P are influenced by the constitution of the compound. By following the method adopted by Brühl in calculating the atomic refractivities, Erfle[1] has obtained the following values for P. $\frac{e}{m}$. 10^{-7}.*

TABLE VI.

Group or atom.	$P\frac{e}{m}10^{-7}$	Group or atom.	$P\frac{e}{m}10^{-7}$
CH_2	5·65	Chlorine . .	6·25
$O=$ (in $>CO$) .	2·01	Bromine . .	5·92
$O-$ (in $-OH$) .	2·51	Iodine . .	3·73
$O<$ (in esters) .	3·53	Fluorine . .	2·2
O (in ethers). .	2·11	Benzene ring .	−7·61
Hydrogen . .	1·60	Ethylenic linkage	−5·03
Carbon . . .	2·45	Acetylene ,,	−1·82

The molecular values of $P.\frac{e}{m}$. 10^{-7} for a substance may be calculated from these atomic values, but the result does not always agree very closely with the number obtained directly from the dispersion of the substance. For example :—

TABLE VII.
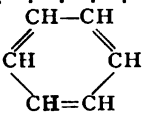
	$P\frac{e}{m}10^{-7}$	
	Observed.	Calculated.
Acetaldehyde . .	13·21	13·31
Acetyl chloride .	17·64	17·96
Propyl chloride. .	24·72	24·80
Ethyl bromide . .	18·33	18·82
Pentane	30·98	31·45
Allyl ethyl ether .	26·18	25·33
,, acetate . .	26·51	25·56
,, alcohol . .	15·93	14·43

[1] Inaugural Dissertation, *Optische Eigenschaften und Elektronen Theorie*, J. A. Barth, Leipzig, 1907.

* The value of $\frac{e}{m}$ is constant, being the ratio of the charge of the electron to its mass. The dispersion interval employed in these calculations was uniformly from H_β to H_γ.

The negative values for the unsaturated linkages are noteworthy, and if it is permissible to interpret this in terms of valency, it would seem that unsaturation either diminishes the number of valency electrons or alters the period of their free vibrations so much that they cease to influence the dispersion in the particular region dealt with.

Also it is remarkable that the juxtaposition of unsaturated groups influences the value of $P\frac{e}{m}10^{-7}$; this is evident from the following comparisons of experimental and calculated values.

	$P\frac{e}{m}10^{-7}$	
	Observed.	Calculated.
Ethyl crotonate . . . . $CH_3CH=CH-\overset{\parallel}{\underset{O}{C}}-OC_2H_5$	29·98	31·21
Ethyl aconitate . . . . $C_2H_5OOC . CH_2-\underset{\underset{COOC_2H_5}{\mid}}{C}=CH-\overset{\parallel}{\underset{O}{C}}-OC_2H_5$	56·3	69·8
Benzene . . . . $\begin{matrix} CH-CH \\ CH \qquad CH \\ CH=CH \end{matrix}$	16·7	9·2 [1]

Some further valuable information of the nature of valency has been obtained by Barlow and Pope from the volume relations of crystalline solids. These investigations have shown that the valency of an atom is proportional to the volume of its sphere of influence,[2] and an attempt has been made by Traube[3] to reconcile this discovery with the electronic view of valency.

[1] With allowance for three ethylenic linkages.

[2] See p. 131.

[3] See p. 135.

This problem of the nature of valency is undoubtedly the most important of those awaiting solution from the chemist. The opinion of chemists seems divided as to whether the electronic theory can be accepted or not. Against its adoption it is urged that the electron is nothing but a figment of the physicists' imagination, and that chemists can derive no real benefit from it. But it may be pertinently asked whether the atom is not equally a figment of the chemists' imagination, and are we to reject this also? At present, however, the electronic theory seems to be the only means by which there is any prospect of attaining further knowledge of the nature of valency, and this circumstance alone should be sufficient recommendation for a thorough trial. At any rate, if we reject it we have nothing else to offer as an adequate substitute. Moreover, the electronic theory offers some mechanical conception of the process of chemical union, and although mechanical ideas are apt to mislead if followed too far, it should be remembered that the chemist has always found them to be peculiarly adapted to his needs. This advantage of the theory is apparent in the scheme which Ramsay has devised[1] for representing the structure of inorganic compounds.

To attempt any further discussion of the adaptability of the electronic theory to chemistry would lead too far into speculation; but apart from that question it is hoped that enough has been said in this chapter to show the importance which the study of physical properties may have for the chemist in the future. If any fresh lines of research have been suggested, the chief endeavour of the author will have been accomplished.

[1] The *Theory of Valency*, Dr. Friend, this series.

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